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MOVING STRIATIONS IN DISCHARGE TUBES.*

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IT IS well known that the current through a Geissler discharge tube, even when maintained by a battery of steady storage cells, may under certain circumstances be unsteady, even regularly intermittent.[1, 2] The conditions governing this intermittence have apparently never been understood or even reproducible.

In the case of neon, Aston and Kikuchi[3] noticed a visible irregular intermittence in a rotating mirror which they attributed in some way to sound waves travelling down the tube.

The present experiments deal in the main with the luminous discharge through argon; certain interesting results have been obtained which seem worth placing on record in a more amplified form than the first preliminary notice.[4]

The apparatus is simple. A straight, clear quartz tube with a bulb blown at one end carries a hot tungsten cathode in the centre of the bulb, and a heavy plane-faced anode at the other end, the distance of separation being about 30 cm. The tube usually used was about 2 cm. in diameter.

In order to reduce gas evolution during working to a minimum, both electrodes were suitably water cooled, while during the

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initial stages of evacuation the whole tube was heated with a blow-pipe. Evacuation was carried out with a mercury-vapor pump, backed with a good oil pump, the usual liquid air-trap being introduced to keep back any mercury vapor. An indication of the pressures employed was given by a Pirani gauge, which had been calibrated against an ordinary McCleod gauge,

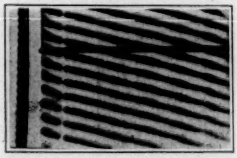
FIG. 1.

the Pirani being preferred for repetition work in view of its rapidity of action and ease in use.

When the discharge is passing in the tube and the argon is pretty pure, the so-called uniform positive column is the main feature. It is this type of discharge which is investigated in these experiments between pressures of about 0.1 to 2 or 3 mm. of mercury.

Under these conditions it is possible to pass quite large currents through the tube, as much as 15 amperes having been

FIG. 2.



safely observed occasionally, the current being drawn from a battery of large lead accumulators.

If the length of the tube be now covered with a fibre sheet carrying a longitudinal narrow cut, to form a slit and then the reflection of the discharge be viewed in a mirror rapidly rotating about an axis parallel to that of the tube, the appearance shown in Figs. 1 and 2 is presented.

The regularity of intermittence is obviously shown up in these photographs.

The horizontal narrow line is a direct photograph of the slit in the mirror at rest and so tilted that the camera views the tube. The side marks are photographs in the rotating mirror of a small quartz-mercury-vapor lamp fed with alternating current of about 50,000 v. from a suitably disposed, valve maintained oscillating circuit.

These timing marks are taken simultaneously by the camera with the discharge tube itself and thus serve the double purpose of giving a time scale on the plate and also ensuring that the camera shutter is so working as to preclude the possibility of a double exposure.

The significance of the sloping lines is clear. They must be produced by a regular sequence of bright flashes moving down the tube with uniform velocity, their distance apart and speed being easily measured from the plate.

Further, the direction of inclination of the lines shows them to be due to flashes travelling from the anode to the cathode. The actual speed of the flashes is dependent on the pressure of the gas, being approximately inversely proportional to the pressure, and varying between 10^3 and 10^4 cm. per sec., or thereabouts, over the range studied. A most significant feature, however, is that whereas pressure changes the velocity very considerably, yet the number present at any instant in the tube very frequently remains the same. This means that under certain conditions, impossible so far to specify, the distance between successive flashes remains constant as the pressure, and consequently the velocity, changes.

It frequently happens, on the other hand, that the simple relation just outlined, regarding the flash separation, does not hold. A small change in current, for example, may cause the flashes to double or treble while still maintaining their slope in the mirror—a point which will be referred to again later.

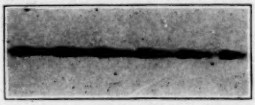
While the mirror rotating about an axis parallel to the axis of the tube gives valuable information about the flash speed, it only gives an indication of the actual shape of the flash. It is clear from the few photographs reproduced here, that sometimes

the flashes are broad and at other times are exceedingly narrow. In general they are broader at higher gas pressures.

It is not very difficult to see the actual shape of these moving flashes. It is only necessary to arrange the axis of the mirror accurately at right angles to the axis of the tube and then to rotate it in such a direction that the reflected image moves in the opposite direction to its actual motion. The speed of the mirror and its distance from the tube can then be adjusted so as to hold the flashes stationary. Photographs taken in this way are reproduced in Fig. 3.

This photograph shows a case where the flashes are single and equally separated in the tube. They are seen to be wedge

FIG. 3.



shaped, convex towards the cathode, with a kind of tail trailing behind. The more or less continuous faint luminous background extending between the flashes is here shown. The photograph reminds one very strongly of the well-known stationary striæ frequently observed in mixtures of gases.

These moving flashes under different discharge conditions have been photographed also when they are doubled or trebled.

Interesting numerical relations not yet explained have been observed between the distances apart of these double and triple flashes.

LUMINOSITY OF THE DISCHARGE.

It was very soon noticed that the amount of light emitted from the tube appeared to be small, considering the energy dissipated within it.

A simple test was, therefore, carried out with only 5 cm. of the tube exposed at a distance of 1 ft. away from a white matt scattering surface. The surface was viewed through a "Lumeter" photometer, using a light filter letting through 5000–5500 Å. With 1 ampere flowing, and a potential of 100 volts on the tube, the intensity of illumination came out to about 0.8 foot-candle. Taking into account the whole length of the

tube, the intensity may be taken as about 5 foot-candles. In view of the intermittent nature of the luminous discharge this was thought to be rather remarkable. A further experiment was performed with a cathode-ray oscillograph used to measure the current through the tube from observations on the potential drop along a small non-inductive resistance in series with it. It emerged that less than 5 per cent. of the total current was fluctuating, the flashes themselves being therefore associated with a very small part of the current, most of it resulting in little, or no, luminosity.

It is not without interest at the present stage to hazard some explanation of these phenomena, although the experiments have not yet gone far enough for anything like certainty.

It had previously been observed that internal ionic oscillations were possible in " soft " thermionic valves, and could be explained in a simple manner.[5]

The theory there put forward is suggestive in the present connection.

Suppose that there is a steady drift of electrons down the tube towards the anode and that when they reach the anode there is at its surface a greater probability of ionization than elsewhere. A sheet of ions will be initiated which will begin to move down the tube towards the cathode, but between this sheet and the anode itself the electric force must be less than previously, so that until the sheet has moved away a certain distance no further ions can be produced. When this certain distance is exceeded a fresh sheet will be produced and the process will be repeated indefinitely, the motion of the new sheets maintaining the motion of their predecessors.

Moreover, it can be seen in a general way why it is possible for the flashes to maintain their individuality and not to decay rapidly in their passage down the tube, for each flash may be regarded as a virtual anode in motion down the tube, fresh ions being formed all the time to take the place of those disappearing by recombination.

It is possible also to explain the production of these flashes in a general way on the supposition that ionization rather than excitation of the atoms is involved. In this case the motion of the flashes would be ascribed to diffusion.

Experiments are now in progress which, it is hoped, will distinguish definitely between these two possible views.

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THE EFFECT OF NON-UNIFORMITY AND PARTICLE SHAPE ON "AVERAGE PARTICLE SIZE."

BY

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ALTHOUGH much has been written on methods for determining particle size, so far little explanation has been offered as to the meaning of "average particle size" when this term is applied to materials composed of particles that are irregular in shape and non-uniform in size. When these important factors are disregarded the term "particle size" often becomes too abstract to be of much use, especially when it is desired to correlate it with some other property of the material. The question that arises is, can the effect of non-uniformity and shape be so taken into consideration that the indefiniteness of "average particle size" is eliminated? To express the problem somewhat differently: If we had a model of a particulate substance composed of blocks of various geometrical shapes and sizes, and if these blocks were sufficiently large so that measurement of their edges, faces, and angles was easily accomplished, could these measurements be taken and converted by mathematical formula into an average diameter that would be definite and useful? The importance of this problem is obvious, for if solution should be found impossible under such ideal conditions, then solution is impossible under all conditions, practical or otherwise. The object at present is to determine how far this problem can be solved. In order to carry out the work systematically, it was felt necessary to divide the paper into two parts: Part I investigates the effect of non-uniformity on particle size, where only the simplest shapes enter; Part II goes into detail in regard to the effect of shape on the particle size of non-uniform materials.

PART I.

EFFECT OF NON-UNIFORMITY ON AVERAGE PARTICLE SIZE.

A non-uniform particulate substance is one in which the constituent particles differ from one another in diameter. Perrott and Kinney[1] were the first investigators to study the effect of

[1] "The Meaning and Microscopic Measurement of Average Particle Size," *Jour. Am. Ceramic Soc.*, 1922, **17**, 327.

non-uniformity on the average diameter, and they were able to show as a consequence that non-uniformity produced "average diameters" that not only differed from the arithmetical mean, but were of considerably more importance than that average. Perrott and Kinney, however, did not develop their ideas to the extent where they were able to show the interesting relationships between the average diameters, nor did they develop the important formulas for mixtures. Furthermore, they made no detailed study of shape and how it affects the various formulas involved.

If non-uniformity brings into existence various average diameters differing from the arithmetical mean, it is important to study these diameters, determine their relationship to one another, and ascertain their advantages and uses. Before proceeding to do this, it will be necessary to define certain terms employed.

The *diameter* of a particle is any straight line passing through the centre of the particle and terminated at the particle boundary. If the particle is a sphere, the length of its diameter is the same in all directions and consequently "diameter" defines "size" and the two terms become synonymous. For any shape other than the sphere, "diameter" ("size") must be carefully defined. For various reasons, which will appear as the subject progresses, "diameter" is preferable to "size." "Average diameter" and "average particle size" are also synonymous terms, the first being preferable to the latter.

An "average diameter" is the diameter of a hypothetical particle which in some particular way represents the total mass of particles. The diameter of the hypothetical particle is always similar to the diameter of any of the individual particles, when all the particles of a given mass are geometrically similar in regard to shape. For instance, if the diameter of the individual particle is equal to the harmonic mean of its three dimensions, then the average diameter is equal to the harmonic mean of the three dimensions of the hypothetical particle. From the preceding definition it is evident that in a non-uniform material numerous average diameters are possible. The list of average diameters will be restricted, however, to only those that are found useful.

The most important factor in the subject of particle size is specific surface, S. Specific surface as customarily defined is the

surface per gram of material. Expressing this in the form of a general equation gives:

$$S = \frac{1}{\rho\left(\frac{\Sigma nv}{\Sigma ns}\right)} \qquad (1)$$

where ρ is density, v and s the volume and surface of the particle of frequency, n.

In Part I only those materials the particles of which are geometrically similar (but non-uniform in size) will be studied. A material composed entirely of spheres, or entirely of cubes, or of any other shape where the ratios of the particle dimensions are maintained constant throughout the mass, is the type inferred. When geometrical similarity exists it follows that if the particle volume is made proportional to the cube of some arbitrary diameter, and the surface proportional to the square of the same diameter, then the proportionality factors are constant for the entire mass of particles. Therefore, in equation 1 we may substitute $v = v'd^3$ and $s = \sigma'd^2$, where v' and σ' are the proportionality constants. For this special class of materials,

$$S = \frac{\sigma'/v'}{\rho\left(\frac{\Sigma nd^3}{\Sigma nd^2}\right)}. \qquad (2)$$

Equation 2 is less general than equation 1. Equation 2 holds, however, for any particle shape, for non-uniformity, and for any fixed diameter that the investigator chooses to take, the only limitation being geometrical similarity. If the material approaches perfect uniformity, the expression $\Sigma nd^3/\Sigma nd^2$ approaches d, hence it follows that $\Sigma nd^3/\Sigma nd^2$ is the average diameter (for geometrical similarity) from which specific surface can be determined. The shape factor is σ'/v'.

Next, restricting the diameter to $6v/s$ and maintaining geometrical similarity gives,

$$S = \frac{6}{\rho\left(\frac{\Sigma nd^3}{\Sigma nd^2}\right)}. \qquad (3)$$

The diameter of a sphere, the edge of a cube and the harmonic mean of the three edges of a rectangular parallelopiped are each

equal to $6v/s$. This diameter is evidently a kind of "natural" one, for its introduction, as will be seen, simplifies matters considerably. The average diameter $\Sigma nd^3/\Sigma nd^2$ is the third in the list given by Perrott and Kinney and will be written, d_3. At infinite uniformity equation 3 reduces to the well-known expression for specific surface, $S = 6/\rho d$.

The next most important average diameter is the one that gives, N, the total number of particles per gram of material. This is the diameter obtained from measurements made with the slit-ultra-microscope.

Since the volume of the average particle in this case is proportional to the average diameter cubed, then,

$$D = \sqrt[3]{\frac{1}{\nu'}\frac{\Sigma nv}{\Sigma n}}. \tag{4}$$

The volume of the average particle is $\nu' D^3$. The proportionality constant, ν', is the shape factor. If we assume geometrical similarity exists then it is easily shown that,

$$D = \sqrt[3]{\frac{\Sigma nd^3}{\Sigma n}}. \tag{5}$$

Restricting equation 5 to the natural diameter, $6v/s$, gives $\nu' = \pi/6$ for spheres, and $\nu' = 1$ for cubes. The particle of average volume is used to determine N in the manner shown in Table I.

Similar to D there is an average diameter, Δ, that represents the particle of average surface. Since the area of the particle of average surface is proportional to the average diameter squared, then,

$$\Delta = \sqrt{\frac{1}{\sigma'}\frac{\Sigma ns}{\Sigma n}}, \tag{6}$$

where σ' is the shape factor; again assuming geometrical similarity gives,

$$\Delta = \sqrt{\frac{\Sigma nd^2}{\Sigma n}}. \tag{7}$$

The surface of the particle of average surface is equal to $\sigma'\Delta^2$. Restricting the equation to $d = 6v/s$ gives $\sigma' = \pi$ for spheres, and $\sigma' = 6$ for cubes. In Table I is given a list of the important

TABLE I.

Average Diameters.	For All Cases.	Uses of the Average Diameters.	Particles Possess No Geometrical Similarity.		Particles Possess Geometrical Similarity.			
			d = Any Diameter of Each Particle.		d = Any Diameter of Each Particle.		d = Any Fixed Diameter for All Particles.	$d = 6\left(\frac{v}{s}\right)$.
			Few Particles.	Many Particles.	Few Particles.	Many Particles.	Few or Many Particles.	Few or Many Particles.
d_1	$\frac{\Sigma nd}{\Sigma n}$	Arithmetical mean	$\nu' = \frac{\Sigma v}{\Sigma nd^3}$	$\nu' = \frac{\Sigma v}{\Sigma n}$	$\nu' = \frac{\Sigma v}{\Sigma nd^3}$	$\nu' = \frac{\Sigma v}{\Sigma n}$	$\nu' = \frac{\Sigma v}{\Sigma \frac{v}{d^3}}$	$\nu' = \frac{k}{216}$
d_2	$\frac{\Sigma nd^2}{\Sigma nd}$	*						$\sigma' = \frac{k}{36}$
d_3	$\frac{\Sigma nd^3}{\Sigma nd^2}$	To determine S when ρ is known						$k = \frac{s^3}{v^2}$ = constant for the mass of particles
d_4	$\frac{\Sigma nd^4}{\Sigma nd^3}$	*						
Δ	$\sqrt{\frac{\Sigma nd^2}{\Sigma n}}$	To determine S when N is known	$\sigma' = \frac{\Sigma s}{\Sigma nd^3}$	$\sigma' = \frac{\Sigma s}{\Sigma n}$	$\sigma' = \frac{\Sigma s}{\Sigma nd^3}$	$\sigma' = \frac{\Sigma s}{\Sigma n}$	$\sigma' = \frac{\Sigma s}{\Sigma \frac{v}{d^3}}$	Rectangular parallelopipeds: d = harmonic mean of its 3 dimensions
D	$\sqrt[3]{\frac{\Sigma nd^3}{\Sigma n}}$	To determine N when ρ is known	$\rho' = \frac{\Sigma w}{\Sigma nd^3}$	$\rho' = \frac{\Sigma w}{\Sigma n}$	$\rho' = \frac{\Sigma w}{\Sigma nd^3}$	$\rho' = \frac{\Sigma w}{\Sigma n}$	$\rho' = \frac{\Sigma w}{\Sigma \frac{v}{d^3}}$	Cubes: d = edge $\nu' = 1$ $\sigma' = 6$
N	$\frac{1}{\rho\nu' D^3}$	The number of particles per gram						Spheres: d = diameter $\nu' = \frac{\pi}{6}$ $\sigma' = \pi$
S	$\frac{\sigma'}{\nu'}\frac{}{\rho d_3}$ $\sigma' \Delta^2 N$	Specific surface; amount of surface per gram						

*See Perrott and Kinney. Equations 8, 9, and 10 hold for all cases.

average diameters and the value of the shape factors under various conditions. The shape factors for any individual particle are v and σ; for a mass of particles, v' and σ'. Though geometrical similarity was assumed in deriving the expressions for the various diameters, it will be shown in Part II that these expressions are applicable to all cases, that is, even where geometrical similarity does not exist.

The amount which the various average diameters differ from one another depends on the uniformity of the material. If the probability curve expresses the relationship between particle size and frequency, then the so-called precision coefficient can be used as a basis for the measurement of uniformity. U, the uniformity coefficient, is derived experimentally from the following equation:

$$U = d_1 \sqrt{\frac{\Sigma n}{2 \Sigma n (d_1 - d)^2}}. \qquad (8)$$

The average diameter, d_1, is introduced for two reasons: First, it makes U an abstract number, independent of magnification and of the unit of length employed. Second, it makes U dependent upon the relative values of the average particle size and the sum of the squares of the "residuals," $\Sigma n(d_1 - d)^2$. An illustration will show the necessity for this dependency. Suppose there exists a pigment having $d_1 = .3$ micron, and particles ranging from .1 to .5 micron. The difference between the largest and smallest particles is .4 micron, and this value being large in comparison with the average, d_1, it follows that U should be small. On the other hand, if amongst a number of marbles a difference of only .4 micron existed between the largest and smallest, this difference being negligible, compared to the size of the marbles, the uniformity should be high. If the distribution curves of these two materials coincided when superimposed, then the uniformity of the pigment would be equal to that of the marbles, if d_1 was not included in equation 8. This undesirable condition is corrected by the introduction of d_1.

When all the particles in a material are equal in size, U becomes infinitely great and the average diameters coincide. As soon as non-uniformity enters, the average diameters separate, and they do this in such a way that certain definite relationships

are always maintained. These relationships are derived from Table I and are:

$$d_1 d_2 = \Delta^2 \tag{9}$$

$$d_1 d_2 d_3 = D^3 \tag{10}$$

$$d_4 > d_3 > \left\{ \begin{matrix} > \\ d_2 = D \\ < \end{matrix} \right\} > \Delta > d_1 \tag{11}$$

Equations 9, 10, and 11 hold for all materials whether their distribution curves follow the probability curve or not. These three equations give all the primary relationships existing between the important average diameters. Knowing this, it becomes possible to write down hypothetical cases and study their peculiarities. Take, for instance, the following:

Average Diameters.	*A*.	*B*.
d_3	.600 micron	.500 micron
D	.416	.416
d_2	.400	.430
Δ	.346	.379
d_1	.300	.334

A and *B* are two particulate materials. If their various average diameters are substituted in equations 9, 10 and 11 no contradictions will appear; therefore, such materials as *A* and *B* could actually exist.

If comparisons are now made between the average particle sizes of *A* and *B* it will be seen in

Comparing the average diameters, d_3, that $A > B$
Comparing the average diameters, D, that $A = B$
Comparing the average diameters, d_1, that $A < B$

The question now arises, which material, *A* or *B*, has the larger particle size. The answer is, that such a question, as it stands, is meaningless. Hence,

When making a particle size comparison of two or more non-uniform particulate substances, it is necessary to state the average diameter used in making the comparison. In addition, a comparison from a single set of similar diameters can give no indication as to the relative values existing between the remaining similar average diameters.

Again, let the following case be considered: Suppose that A and B are two samples of zinc oxide (density 5.7) with average diameters the same as those just given. If these materials are dispersed, put into suspension, and their sizes determined by means of a slit-ultra-microscope (which can give only average diameter D) it will be found that each substance has an average diameter of .416 micron. Now it seems to be universally assumed that if two particulate substances have the same average particle size, then they must have equal specific surfaces. That this conclusion is not always correct, is easily shown. Specific surface is determined from d_3; it cannot be determined from D. Assuming geometrical similarity and $d = 6v/s$, then.

$$\text{Specific surface of } A = \frac{6}{5.7 \times .6} = 1.75 \text{ sq. metres per gram;}$$

$$\text{Specific surface of } B = \frac{6}{5.7 \times .5} = 2.10 \text{ sq. metres per gram.}$$

The fact that the D diameters of A and B are equal does not necessitate equal d_3 diameters. The only necessary requirements are, that the values of D and d_3 introduce no contradictions in equations 10 and 11.

MIXTURES OF NON-UNIFORM MATERIALS.

It is apparent that a single non-uniform material can be treated as a mixture of two or more fractions of various particle sizes; that is, there is nothing fundamentally different between a non-uniform substance and a mixture of non-uniform substances. Any formula applicable to the one is also applicable to the other. For experimental reasons, however, it is more convenient to write the formulas for mixtures as functions including the weights of the various fractions involved. This gives a means for calculating the average particle size of mixtures from the particle size and weights used of the original materials. When mixtures are indicated, the symbols are written, $\overline{D}$, $\overline{d_3}$, $\overline{N}$, etc. The weight of a fraction is w. The formulas for mixtures are given in Table II; they are derived from their corresponding values in Table I.

Equation 8 (page 718) is based on the probability curve. There is no objection, however, to applying this equation to any set of measurements of particle diameter and of frequency, regardless of the form of the distribution curve they produce.

TABLE II.

Formulas for mixtures possessing geometrical similarity. d = any fixed diameter. For values of σ', ν', and σ'/ν' refer to corresponding formulas in Table I.

(1)	$\overline{d}_1 = \dfrac{\Sigma \dfrac{d_1 w}{D^3}}{\Sigma \dfrac{w}{D^3}}$	(2)	$\overline{d}_2 = \dfrac{\Sigma \dfrac{w}{d_3}}{\Sigma \dfrac{w}{d_2 d_3}}$
(3)	$\overline{d}_3 = \dfrac{\Sigma w}{\Sigma \dfrac{w}{d_3}}$	(4)	$\overline{d}_4 = \dfrac{\Sigma d_4 w}{\Sigma w}$
(5)	$\overline{\Delta} = \sqrt{\dfrac{\Sigma \dfrac{w}{d_3}}{\Sigma \dfrac{w}{D^3}}}$	(6)	$\overline{D} = \sqrt[3]{\dfrac{\Sigma w}{\Sigma \dfrac{w}{D^3}}}$
(7)	$\overline{S} = \dfrac{\sigma'/\nu'}{\rho \overline{d}_3}$	(8)	$\overline{N} = \dfrac{1}{\rho \nu' \overline{D}^3}$

When this is done in the case of mixtures, the value of U obtained is the uniformity of the mixture. It is justifiable to call U a uniformity coefficient, for it has all the necessary qualifications: (a) It becomes infinite when all the particles are of equal size; (b) it becomes zero when no two particles are equal in size; (c) it gives proper weight to the frequency of each size; (d) it takes into consideration the average diameter, d_1. The application of equation 8 to mixtures necessitates the following definition:

The uniformity of a mixture of materials is equal to the uniformity of an imaginary substance conforming to the probability curve and having the same d_1 diameter and the same value for the ratio, $\Sigma n/\Sigma n(d_, - d)^2$ as that of the mixture.

The adoption of this definition makes equation 8 entirely general. Like the equations in Table II, equation 8 is more useful for mixtures when expressed as a function of w:

$$\overline{U} = \overline{d}_1 \sqrt{\frac{\Sigma \dfrac{w}{D^3}}{\Sigma \left\{ \dfrac{w}{D^3} \left[\dfrac{d^2_1}{U^2} + 2 (\overline{d}_1 - d_1)^2 \right] \right\}}} \qquad (12)$$

Equation 12 is restricted to geometrical similarity; d may be any fixed diameter.

Briefly summarizing the work covered so far, it has been found: (a) That there is no general average particle size; (b) particle size must be given as some definite average diameter. Which average diameter is to be selected will depend upon the use to which it is to be put; (c) non-uniformity introduces complexity but no insurmountable difficulties so long as the mass of particles possess geometrical similarity; (d) the natural diameter of a single particle is $6v/s$.

PART II.

EFFECT OF SHAPE ON AVERAGE PARTICLE SIZE.

In Part I the definition of a non-uniform particulate substance was given as a material containing particles that differed from one another in diameter. If the particles possessed geometrical similarity (as they were supposed to do in Part I), the effect of shape on uniformity could be neglected. It is now necessary to study the effect of geometrical dissimilarity on this particular aspect of the subject. If all the particles of a given mass are equal in size and similar in shape, then perfect uniformity should be expected; but if the particular shape is not that of a sphere then it becomes possible to obtain various lengths for the diameters of the particles. Suppose, then, that our method of measurement were such that similar particle diameters could not be obtained for all the particles, then the material would show from its measurement a perceptible degree of non-uniformity.

A case which seems even more paradoxical than the preceding is one where the particles vary in volume but remain constant in diameter, so in spite of this apparent non-uniformity they show perfect uniformity from their measurements. Let us suppose that the particles are rectangular parallelopipeds and that their three dimensions can be measured; also let the harmonic mean of the three dimensions be taken as the diameter or "size" of the particle. The harmonic mean is $6v/s$; any series with a constant volume-to-surface ratio will, according to this hypothesis, have perfect uniformity. For example, 1/2, 2/4, 4/8. Here the volumes range from 1 to 4, but since the harmonic means are equal, all the particles have the same "size." This case can

be pushed to extremes so that eventually we have infinitely small particles equal in size to infinitely large ones.

On account of this unfortunate condition it might seem advisible to abandon the use of the harmonic mean. This cannot be done, however, for when it is desired to determine specific surfaces, the particle volume alone is insufficient and we must have for "size" a diameter containing the volume-to-surface ratio. The harmonic mean fulfills this condition. All the particles in this particular series have the same specific surface. Therefore, they must have something in common, and that something is their harmonic mean diameter.

These unusual cases, however, are never encountered in practice and need be given no further consideration; they are included simply to emphasize the fact that the uniformity coefficient is always in reference to the particular diameters of the particles measured.

The uniformity of a single material is determined from equation 8. As shape does not enter here, equation 8 is applicable to all cases, even where no geometrical similarity exists. Equation 12, however, is for geometrical similarity only; for geometrical dissimilarity it is modified as follows:

$$\overline{U} = \overline{d}_1 \sqrt{\frac{\Sigma \frac{w}{(\nu' D^3)}}{\Sigma \left\{ \frac{w}{(\nu' D^3)} \left[\frac{d^2_1}{U^2} + 2 (\overline{d}_1 - d_1)^2 \right] \right\}}}, \qquad (13)$$

where in practice the term $(\nu' D^3)$ is determined with the slit-ultra-microscope. In case the various fractions are of different composition, the densities must be introduced in equations 12 and 13. This is done by putting ρD^3 for D^3 and $\rho \nu' D^3$ for $\nu' D^3$.

We now come to the most important step in the development and simplification of the present subject. The factor $\nu' D^3$ in actual practice can be experimentally determined, as stated, with the slit-ultra-microscope.

$$\nu' D^3 = \frac{\Sigma \nu d^3}{\Sigma n} = \frac{\text{Total Volume of Particles}}{\text{Total Number of Particle}} =$$

the volume of the particle of average volume.

The particle of average volume is purely hypothetical as far as its existence is concerned. Any definite shape, therefore, may

be assigned to it. Colloid chemists always make $\nu' = \pi/6$, that is, they treat this particle as a sphere and calculate D on that basis. An arbitrary value, however, could just as readily have been given to D, and ν' determined accordingly.

The slit-ultra-microscope deals with only one average diameter, that is, with D; it cannot provide a means for studying any of the other average diameters. In order to investigate all the average diameters, it is necessary to develop some other means, such as direct microscopic measurement. Let it be assumed that such a method has been developed.

If the method of the colloid chemist is now adopted by assigning arbitrary values to ν' and σ', it will be found that the average diameters from direct measurement will be functions not only of n and d, but also of ν and σ. Since ν and σ cannot be determined in actual practice, this method becomes impractical. Our one means of escape from this difficulty is to assign to the average diameters arbitrary values (not numerical, of course) in which ν and σ do not appear. This procedure is quite permissible as long as no attempt is made to fix the values of ν' and σ' at the same time. In Part I the values for the average diameters were determined on the basis of geometrical similarity. It is permissible to use these same values here in the absence of geometrical similarity, provided arbitrary values are not assigned to ν' and σ'.

This idea was carried out in the construction of Table I. In this table the values of the average diameters are the same for both cases, that is, where geometrical similarity exists and also where it does not exist. The values of the shape factors differ, however, in each case. As the shape factors do not enter into the three fundamental equations, 9, 10, and 11, on the present plan, these equations hold for all cases. If the opposite plan had been adopted, by giving definite values to ν' and σ', equations 9 and 10 would still hold, but it would be difficult or impossible to prove the validity of 11.

Table II was worked out on the basis of geometrical similarity. In Table III are given the formulas for mixtures where geometrical similarity is absent.

The question was asked at the beginning of Part I whether it was possible to take a series of blocks, of various sizes and shapes, obtain their measurements, and from these measurements

determine an average diameter that would be definite and useful. It is now possible to see how far this question can be answered. Let the following example be taken: 1 rectangular parallelopiped, $1 \times 1 \times 4$; 1 cube with an edge, 2; 1 sphere with a diameter of 3. Let the weight of the model be 1 gram; its density, therefore, will be .0383. As geometrical similarity is absent nothing can be

TABLE III.
Mixtures.

No geometrical similarity. For any particle diameter, fixed or otherwise.

(1) $$\bar{d}_1 = \frac{\Sigma \frac{d_1 w}{(\nu' D^3)}}{\Sigma \frac{w}{(\nu' D^3)}}$$

(2) $$\bar{d}_2 = \frac{\Sigma \frac{d_1 d_2 w}{(\nu' D^3)}}{\Sigma \frac{d_1 w}{(\nu' D^3)}}$$

(3) $$\bar{d}_3 = \frac{\Sigma \frac{D^2 w}{(\nu' D^3)}}{\Sigma \frac{\Delta^2 w}{(\nu' D^3)}}$$

(4) $$\bar{d}_4 = \frac{\Sigma \frac{d_4 D^2 w}{(\nu' D^3)}}{\Sigma \frac{D^2 w}{(\nu' D^3)}}$$

(5) $$\bar{\Delta} = \sqrt{\frac{\Sigma \frac{\Delta^2 w}{(\nu' D^3)}}{\Sigma \frac{w}{(\nu' D^3)}}}$$

(6) $$\bar{D} = \sqrt[3]{\frac{\Sigma \frac{D^3 w}{(\nu' D^3)}}{\Sigma \frac{w}{(\nu' D^3)}}}$$

(7) $$\bar{S} = \Sigma \frac{(\sigma'/\nu') w}{\rho d_3 \Sigma w}$$

(8) $$\bar{N} = \frac{1}{\rho \left(\frac{\Sigma w}{\Sigma \frac{w}{(\nu' D^3)}} \right)}$$

(9) $$\bar{\nu} = \frac{\Sigma w}{\Sigma \frac{w D^3}{(\nu' D^3)}}$$

(10) $$\bar{\sigma} = \frac{\Sigma \frac{\sigma' \Delta^2 w}{(\nu' D^3)}}{\Sigma \frac{\Delta^2 w}{(\nu' D^3)}}$$

In practice the factor $(\nu' D^3)$ can be determined with the slit-ultra-microscope.

gained by taking a fixed particle diameter such as $6v/s$. Any convenient measurement, therefore, will be taken as particle diameter.

In the case of the rectangular parallelopiped the unit edge will be taken as the diameter; the edge of the cube and the diameter of the sphere, as their diameters. The average diameters are calculated from the formulas given in Table I, column 2; the

shape factors, in column 4. Substituting the value of d_3 in equation 2 gives a specific surface of 70.27. As the model weighs a gram, Σs must also give the specific surface and, as shown in the table, has the value of 70.27. The cube of D when

TABLE IV.

No Geometrical Similarity. d = Any Diameter.

	n	d	nd	nd^2	nd^3	nd^4	$n(d_1-d)^2$	s	v
Parallelopiped	1	1	1	1	1	1	1	18	4
Cube	1	2	2	4	8	16	0	24	8
Sphere	1	3	3	9	27	81	1	28.27	14.15
	$\Sigma n=3$		$\Sigma nd=6$	$\Sigma nd^2=14$	$\Sigma nd^3=36$	$\Sigma nd^4=98$	$\Sigma n(d_1-d)^2=2$	$\Sigma s=70.27$	$\Sigma v=26.15$

$$d_1 = \frac{\Sigma nd}{\Sigma n} = 2.00$$

$$d_2 = \frac{\Sigma nd^2}{\Sigma nd} = 2.33$$

$$d_3 = \frac{\Sigma nd^3}{\Sigma nd^2} = 2.57$$

$$d_4 = \frac{\Sigma nd^4}{\Sigma nd^3} = 2.72$$

$$\Delta = \sqrt{\frac{\Sigma nd^2}{\Sigma n}} = 2.16$$

$$D = \sqrt[3]{\frac{\Sigma nd^3}{\Sigma n}} = 2.29$$

Let weight of sample = 1 gram.

Then $\rho = \frac{1}{26.15} = .0383$

$$\nu' = \frac{\Sigma v}{\Sigma nd^3} = .727$$

$$\sigma' = \frac{\Sigma s}{\Sigma nd^3} = 5.02$$

$$\frac{\sigma'}{\nu'} = 6.90$$

$$S = \frac{\sigma'/\nu'}{\rho d_3} = 70.27; \quad S = \sigma' \Delta^2 N = 70.27; \quad S = \frac{\Sigma s}{1 \text{ gram}} = 70.27$$

$$N = \frac{1}{\rho \nu' D^3} = 3; \quad U = d_1 \sqrt{\frac{\Sigma n}{2 \Sigma n (d_1 - d)^2}} = 1.73$$

(9) $$\frac{2.00}{d_1} \times \frac{2.33}{d_2} = \frac{4.66}{2}$$

(10) $$\frac{4.66}{\Delta^2} \times \frac{2.57}{d_3} = \frac{12}{D^3}$$

(11) $$\frac{2.72}{d_4} > \frac{2.57}{d_3} > \frac{2.33}{d_2} > \frac{2.29}{D} > \frac{2.16}{\Delta} > \frac{2.00}{d_1}$$

used in the formula in Table I gives $N = 3$. The fundamental expressions 9, 10, and 11 given in Part I are also shown to hold here for the average diameters. U is found to be 1.73.

It can be seen that the average diameters are definite in so far as they can be expressed by definite mathematical formulas, but

their actual numerical values depend on the particular diameters chosen for measurement of the individual particles. The complete usefulness of the average diameters can be attained only when the shape factors v' and σ' are known.

So much for the purely theoretical side of the subject. The next question to be investigated is, how much of what has preceded can be applied in actual practice. Methods for determining particle size comprise two distinct types, those giving a single measurement and those that give particle distribution curves from which any of the average diameters can be determined. The first type includes (*a*) the slit-ultra-microscopic method, (*b*) the counting chamber method, (*c*) obscuring methods and (*d*) the Tyndallometer. Methods (*a*) and (*b*) are fundamentally the same and give $v'D^3$. Just what relationship exists between the measurements made by methods (*c*) and (*d*) and the average diameters listed in Table I would be difficult to say.

The methods that give the "smoothest" distribution curves are (1) the photomicrographic method proposed by the author [2] and (2) Oden's [3] settling method, including its various modifications. In (1) a photomicrograph of the particles is made and projected on a screen (by means of a lantern) where measurement is made with a millimetre rule. In order not to select any particular particle diameter in preference to any other, only the horizontal diameter through the centre of the image is used. Particle distribution curves are obtained in this manner, in which frequency, n, is plotted against the horizontal particle diameter, d, and from these measurements all the average diameters can be calculated. It is impossible, however, to determine the shape factors for a horizontal diameter of a particle of unknown shape, volume, and orientation, but when necessary, $v'D^3$ can be found ultra-microscopically, and as D^3 is $\Sigma nd^3/\Sigma n$ the factor v' is easily obtained. Unfortunately there is no method, similar to the ultra-microscopic method, for getting $\sigma'\Delta^2$, consequently σ' cannot be determined.

Exactly the same conclusions are drawn from an analysis of Oden's method. Oden uses as the abscissa of his distribution

[2] JOUR. FRANK. INST., Nov., 1921.

[3] "On Clays as Disperse Systems," Sven Oden, *Trans. Faraday Soc.*, 17, p. 327, 1922.

curve the "effective radius" and defines this term as the radius of an imaginary sphere of the same material which would sink in water with the same velocity as the particle in question. From the effective radii and their respective frequencies all the average diameters can be obtained according to the formulas given in Table I, but it must be borne in mind that the numerical values of these average diameters will be different if the material is measured by the photomicrographic method. Oden uses the effective diameter as the diameter of the particle; the photomicrographic method employs the horizontal diameter (as a rule, though it is not restricted to any particular diameter), consequently the values for the average diameters *cannot* be the same for both methods. This illustrates the relative unimportance of average diameters, for their values always depend to a certain extent on the method of measurement.

On the other hand, the really important factors are N or $v'D^3$ and S, for these have fixed values for any given material and are totally independent (theoretically) of the methods of measurement.

How to measure σ' is the important unsolved problem in the subject of particle-size determination. When this stumbling-block is finally removed, a great step in advance will have been made. The solution will probably be found in an adsorption method, that is, the surface per gram, $\sigma'\Delta^2 N$, will be measured from the amount of some material of monomolecular thickness adsorbed upon it. In the meantime, however, we must use what information we have in as practical a manner as possible. This means that wherever it is feasible geometrical similarity must be assumed, and that the particle diameter must be considered equal to $6v/s$. This makes $\sigma'/v' = 6$, and as v' can be determined with the use of the slit-ultra-microscope the value of σ' is easily obtained. These assumptions introduce a certain amount of error, but if they are applied judiciously the error caused by them is probably no greater than the experimental errors involved. If the particles are noticeably acicular or tabular, geometrical similarity should still be assumed, but the diameter $6v/s$ must be determined, when possible, for each particle from microscopical measurements.

SUMMARY OF PART II.

In Part II the effect of shape on uniformity is considered. The use of the formulas of the average diameters obtained on the basis of geometrical similarity is adopted for all cases of geometrical dissimilarity. It is shown that this step not only simplifies matters, but is permissible when arbitrary values are not assigned to the shape factors. Formulas for mixtures are given covering all cases. A hypothetical model consisting of three particles of known dimensions is studied, the average diameter, the shape factors, and S, N, and U determined. The practical application of this work is discussed.

Spectra of High-frequency Discharges in Super-vacuum Tubes. R. W. WOOD and A. L. LOOMIS. (*Nature*, Oct. 8, 1927.)—During the summer just passed the authors made a further study of the results obtained by Kirchner and by Gill and Donaldson showing that a brilliant discharge is given by a tube exhausted to a non-conducting vacuum, provided that the excitation be applied through external electrodes and that the frequency be that of a six- or seven-metre wave. Under these conditions even a low voltage suffices. The tubes of the American workers were "drastically" cleaned, dried and exhausted with a molecular pump, the walls being heated. Through the vacuum thus reached an induction coil giving a two-inch spark sent no discharge. When, however, an oscillating circuit with wave-length of three metres was connected to external tinfoil electrodes a brilliant blue discharge appeared. This showed the hydrogen spectrum. If the pump continued to exhaust the tube with the blue discharge this gradually disappeared and was replaced by "the olive-green discharge characteristic of pure oxygen, while the tube walls phosphoresced with a very brilliant ruby-red light." Further pumping and excitation made the oxygen spectrum derived from the previous discharge to disappear. A pair of prominent carbon lines alone persisted from many lines of that element that had occurred along with the oxygen lines. The red phosphorescence above described manifested itself with tubes of quartz, soft glass, and pyrex glass. One of the authors using a tube that showed the red effect only feebly under excitation by a seven-metre wave-length found that the application of a thirty-metre wave-length caused a much brighter glow. "Using one electrode only, we found that a magnet brought close to the walls, caused a concentration of the red glow on the near side of the tube, the deflection of whatever caused the phosphorescence of the glass indicating negative electrons moving away from the electrode. At the other end of the tube, the magnet repelled whatever caused the glow to the further wall of the tube, indicating electrons moving toward the electrode. We believe that phosphorescence is associated in some way with the presence of positive ions of oxygen but the exact mechanism of its production has not been ascertained." G. F. S.

X-ray Diffraction in Liquids. C. V. RAMAN and C. M. SOGANI. (*Nature*, Oct. 8, 1927.)—A marked difference has been found in the haloes obtained by applying X-rays to aromatic liquids according to the "form, position and mass of the substituent groups which replace the hydrogen atoms in benzene. Ortho-, para- and meta-compounds are readily distinguished by their X-ray liquid haloes." A reproduction of the diffraction haloes of aniline and nitrobenzene is given in which the white spot in the centre is larger and more diffuse for the latter compound. The halo of mercury agrees with predictions based on its having the smallest compressibility of all known liquids. G. F. S.

INTENSIFICATION OF THE LATENT IMAGE ON PHOTOGRAPHIC PLATES AND FILMS.

II. THE DECOMPOSITION OF HYDROGEN PEROXIDE AND THE MECHANISM OF LATENT IMAGE INTENSIFICATION.*†

BY

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IN THE preceding paper [1] some interesting facts concerning the effect which was called the intensification of the latent image by hydrogen peroxide and some other substances were presented.

It had previously been proposed by Dr. S. E. Sheppard and one of us [2] that the effect of hydrogen peroxide in producing latent fog was one of chemiluminescence; that the hydrogen peroxide in being catalytically decomposed by the sensitivity specks in the silver halide grain [3, 4, 5] gives off a radiation of short wave-length which tends photochemically to decompose the silver halide, thus enlarging the sensitivity specks to developable size.

This hypothesis was also found in a general way to explain the facts of the intensifying action of hydrogen peroxide on the

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† Presented in abstract at the regional meeting of the Am. Chem. Soc., at Niagara Falls, Jan., 1926.

[1] E. P. Wightman and R. F. Quirk, JOUR. FRANK. INST., **203**, 261 (1927).

[2] S. E. Sheppard and E. P. Wightman, *Ibid.*, **195**, 337 (1923).

[3] Lüppo-Cramer, "Kolloidchemie u. Photographie," Theodor Steinkopff, Dresden u. Leipzig, I Auf., 1908; II Auf., 1921; F. F. Renwick, *J. Soc. Chem. Ind.*, **39**, 156 (1920); T. Svedberg, *Phot. J.*, **62**, 186 (1922); F. C. Toy, *Phil. Mag.*, **44**, 352 (1922); W. Clark, *Brit. J. Phot.*, **70**, 763 (1923); *Phot. J.*, **63**, 230 (1923); *Ibid.*, **64**, 364 (1924); Sheppard, Trivelli and Wightman, *Trans. Faraday Soc.*, **19**, 296 (1923); Sheppard, Wightman and Trivelli, JOUR. FRANK. INST., **196**, 653, 779 (1923).

[4] S. E. Sheppard, *Colloid Symposium Monograph*, **3**, 76 (1925); *Phot. J.*, **65**, 380 (1925).

[5] S. E. Sheppard, A. P. H. Trivelli and R. Loveland, JOUR. FRANK. INST., **200**, 51 (1925); A. P. H. Trivelli and S. E. Sheppard, *J. Phys. Chem.*, **29**, 1568 (1925); S. E. Sheppard, A. P. H. Trivelli and E. P. Wightman, *Phot. J.*, **67** (1927).

latent image.[1, 6] It was suggested further[6] that not only developable but also undevelopable latent image is produced by light, that the hydrogen peroxide carries the former over into the latter, and in addition makes its normal portion of grains developable.

W. Clark[7] attacked the chemiluminescence hypothesis, apparently with justification, on the ground that hydrogen peroxide, in the presence of a catalyst, is much more rapidly decomposed in alkaline than in acid solutions,[8] and so a greater chemiluminescence effect should be expected with alkaline solution, whereas Sheppard and Wightman had found[2] that the action of acid H_2O_2 was somewhat greater than that of the alkaline solution.

After reviewing the literature of the action of hydrogen peroxide on the photographic plate to produce latent fog, Clark proposed a chemical hypothesis, which he has since admitted to be unsound[9]; although he still maintains that the action is purely chemical, he suggests no definite mechanism of the action.

The object of the present work was to discover, if possible, the underlying mechanism of latent image intensification. We do not propose to deal specifically with the action of hydrogen peroxide on the unexposed plate to produce latent fog, but we infer, for reasons which will appear later, that the mechanism of this is quite similar to that of latent image intensification, the difference being merely one of degree and not of kind.

As to the sensitivity and latent image specks in high-speed emulsions, Sheppard has shown[4] that the former consist largely of Ag_2S. It also seems to be fairly well established[5] that the latent image specks contain free silver as well as silver sulphide.

We believe that the sensitivity spots also contain some silver in addition to silver sulphide. This would behave in the same way toward hydrogen peroxide as the silver in the latent image, but the effect would not be so marked. How could this Ag be present in the sensitivity speck? Two simple explanations offer themselves. First, in the process of emulsion-making some slight decomposition of the Ag halide, or even of the $AgNO_3$ prior

[6] E. P. Wightman, A. P. H. Trivelli, and S. E. Sheppard, JOUR. FRANK. INST., **200**, 335 (1925).

[7] W. Clark, *Brit. J. Phot.*, **70**, 763 (1923).

[8] G. Bredig and M. von Berneck, *Z. Physik. Chem.*, **31**, 258 (1899).

[9] W. Clark, *Phot. J.*, **66**, 78 (1926).

to precipitation, may occur in the presence of gelatin or a trace of some easily oxidizable organic matter. Secondly, emulsions and plates or films are seldom prepared in absolute darkness. Certain parts of the process must be watched, and the plates or films must be inspected and packed. The exposure to safe lights, while slight and not sufficient to produce developable latent fog, may very well cause a slight photochemical decomposition of the Ag halide, either in the neighborhood of the already formed Ag_2S specks, or, less likely, at some distance from them.[5] Certainly excessive exposure to the safe light will cause formation of developable latent fog,[10] and it is reasonable to suppose that intermediate stages could result, as suggested elsewhere[6] for ordinary white light exposures.

Since the silver bromide in plates and films is precipitated in a solution containing excess of potassium bromide, it is safe to say that, even after the emulsion has been washed, there is, besides the gelatin and the silver halide grains containing sensitivity specks, more or less potassium bromide. At any rate, this is present in the plates which we have used, because, when they were bathed in a solution of silver nitrate, a cloud of silver halide gradually formed in the solution.

On looking over the work of Bray and Livingston[11] on the catalytic decomposition of hydrogen peroxide in solutions containing hydrogen and bromide ions, it occurred to us that here might be the source of a partial explanation of the intensification of latent image phenomenon.

In addition to this, Dr. K. C. D. Hickman, of this laboratory, has recently proposed[12] a new chemical mechanism for latent image formation which gives us a further possible clue to the hydrogen peroxide action.

We shall first consider the decomposition of hydrogen peroxide under the complicated conditions existing in the photographic plate.

[10] C. E. K. Mees and J. K. Baker, *Phot. J.*, **47**, 267 (1907); Wightman, Trivelli, and Sheppard, *J. Phys. Chem.*, **27**, 1 (1923); M. L. Dundon and J. I. Crabtree, *Amer. Phot.*, **20**, 378, 438 (1926).

[11] W. C. Bray and R. S. Livingston, *J. Am. Chem. Soc.*, **45**, 1251 (1923); R. S. Livingston and W. C. Bray, *Ibid.*, **45**, 2048 (1923).

[12] K. C. D. Hickman, *Phot. J.*, **67**, 34 (1927).

THE DECOMPOSITION OF HYDROGEN PEROXIDE IN SOLUTIONS OF GELATIN-SILVER SOL AND OF GELATIN-SILVER SULPHIDE SOL AND IN THE PRESENCE OF HYDROGEN AND BROMIDE IONS.

The well-known fact that acids, especially strong acids, diminish the activity of pure colloidal metals as catalysts for the decomposition of hydrogen peroxide, and that alkalies tend to increase the activity,[8, 13, 14] has, as we have said, been cited by Clark[7] as an argument against the chemiluminescence hypothesis[2, 6] of hydrogen peroxide action on the photographic emulsion to produce latent fog.

One reason for the lessened activity of the sol in acid solution is the fact observed by MacIntosh,[15] Spear[14] and others, that colloidal silver dissolves in the acid hydrogen peroxide. It even dissolves to some extent in alkaline solutions they found. MacIntosh states that colloidal silver catalyzes the decomposition of hydrogen peroxide in acid and neutral solutions until it is dissolved.[16] This fact, the solution of the Ag catalyst, is of considerable importance and will be considered later.

Schöne,[17] in 1879, noticed that hydrogen peroxide was catalytically decomposed in a solution of potassium iodide. Bray and Livingston,[11] and very recently Livingston,[18] have made a very careful study of the catalytic decomposition of H_2O_2 in dilute solutions in the presence of H^+ and Br^- ions, K^+ and (SO_4^{--}) ions also being present. The decomposition in a steady state was found to obey a modified monomolecular reaction law. The modification consisted in taking into account the activity coefficient of hydrobromic acid. Prior to the steady state condition the two following reactions take place:

$$H_2O_2 + 2Br^- + 2H^+ = Br_2 + 2H_2O;\ \triangle F^\circ_{298} = -31{,}483 \text{ cals.}, \quad (1)$$

$$H_2O_2 + Br_2 = O_2 + 2Br^- + 2H^+;\ \triangle F^\circ_{298} = -18{,}697 \text{ cals.}, \quad (2)$$

[13] G. Bredig and K. Ikeda, *Z. physik. Chem.*, **37**, 5 (1901); I. S. Telatov, *J. Russ. Phys. Chem. Soc.*, **39**, 1145 (1908).

[14] E. B. Spear, *J. Am. Chem. Soc.*, **30**, 195 (1908).

[15] D. MacIntosh, *J. Phys. Chem.*, **6**, 15 (1902).

[16] It should be noted that when acid H_2O_2 is added to a $AgNO_3$ solution, no precipitation of Ag takes place. When KBr is also added in slight excess, cream-colored AgBr precipitates and does not darken in fairly strong daylight.

[17] E. S. Schöne, *Ann. Chem.*, **195**, 228 (1879).

[18] R. S. Livingston, *J. Am. Chem. Soc.*, **48**, 45 (1926).

The sum of these gives

$$2H_2O_2 = 2H_2O + O_2;\ \Delta F^\circ_{298} = -50{,}180 \text{ cals.}^{19} \qquad (3)$$

"*The transformation of bromide to bromine is favored by high concentration of hydrogen and bromide ions,*[20] and that of bromine to bromide by low concentration of these. However, both reactions can be demonstrated at a single intermediate concentration of hydrogen ion by starting with bromine at zero concentration in one case and at high concentration in the other."

At the start (1) predominates, but as a greater and greater amount of Br_2 is formed (2) takes place more and more rapidly until these reactions balance each other and (3) becomes the only measurable reaction.

On treating a photographic plate with H_2O_2 in acid solution, we do not have the simple conditions as just outlined. We have to consider what effect the gelatin, the latent image (Ag_2S and Ag) and the soluble bromide have on the decomposition at different H-ion concentrations. Later we shall also consider the effect of H_2O_2 under these conditions on the Ag-Ag_2S specks.

First of all then, we wished to know whether or not the decomposition of alkaline H_2O_2, under the conditions similar to those in the plate, is considerably greater than of acid H_2O_2 under like circumstances.

Without making extensive rate measurements, as the former workers have done, we have endeavored to determine the effect of the various factors at different H-ion concentrations on the decomposition of H_2O_2 during some arbitrary period, say an hour's time.

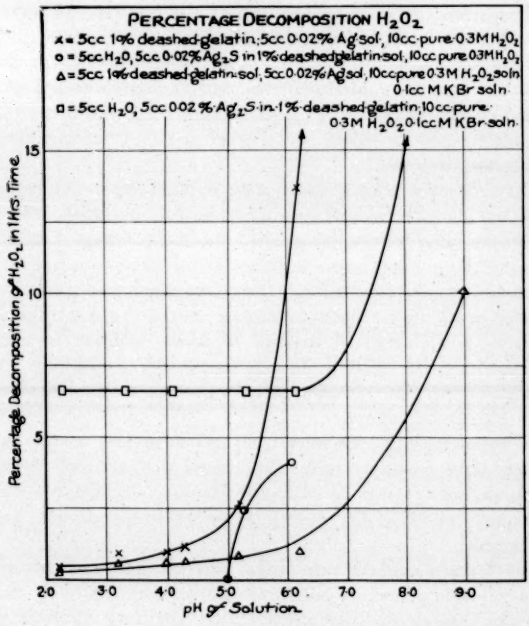
We have found in our work that the presence of gelatin (0.25 per cent.) and of soluble bromide, together with the Ag or Ag_2S catalyst, do not greatly alter the fact of more rapid decomposition of H_2O_2 in alkaline than in acid solution. The actual amount of decomposition in an hour's time at any given pH differs, however, somewhat according to whether Ag or Ag_2S is used, and to whether or not soluble bromide is present. (Fig. 1.)

[19] *Cf.* G. N. Lewis and M. Randall, "Thermodynamics," pp. 485 and 492, McGraw-Hill Book Co., N. Y., 1923; *J. Am. Chem. Soc.*, **36**, 1964 (1914).

[20] Italics are ours and the importance of this statement will appear later.

The Silver Sol.—The Ag sol in our experiments was prepared several years ago by S. E. Sheppard in this laboratory by the Carey-Lea alkaline dextrin method and freed of salts by dialysis. It had a pH of about 6.0 to 6.4 and contained about

FIG. 1.


PERCENTAGE DECOMPOSITION H_2O_2
x = 5cc 1% deashed gelatin, 5cc 0·02% Ag sol, 10cc pure 0·3M H_2O_2
o = 5cc H_2O, 5cc 0·02% Ag_2S in 1% deashed gelatin sol, 10cc pure 0·3M H_2O_2
Δ = 5cc 1% deashed gelatin sol, 5cc 0·02% Ag sol, 10cc pure 0·3M H_2O_2 soln. 0·1cc M KBr soln.
□ = 5cc H_2O, 5cc 0·02% Ag_2S in 1% deashed gelatin, 10cc pure 0·3M H_2O_2 0·1cc M KBr soln.
Percentage Decomposition of H_2O_2 in 1 Hrs. Time.
15
10
5
2·0
3·0
4·0
5·0
6·0
7·0
8·0
9·0
pH of Solution.

0.02 g. of Ag per 100 c.c. After mixing with the gelatin and H_2O_2 solutions the Ag concentration was about 0.005 per cent.

The Silver Sulphide Sol.—The Ag_2S sol was prepared by dissolving 0.685 g. of $AgNO_3$ in 1 litre of a 1 per cent. gelatin solution and passing H_2S into this for a few minutes. The solution was then freed of excess H_2S by bubbling CO_2 through it for several hours. The sol thus formed was very stable and contained about 0.02 g. Ag_2S per 100 c.c.

The Hydrogen Peroxide.—The H_2O_2 solutions used in our decomposition experiments were prepared by diluting portions of a very pure approximately 15 per cent. solution of H_2O_2 obtained from the laboratory of Professor Maas, at McGill University.

The Method of Determining the Amount of Hydrogen Peroxide Decomposition.—The permanganate method was used for determining the concentrations of hydrogen peroxide, or, rather, the degree of decomposition in our experiments. Owing to the presence of gelatin, colloidal silver or silver sulphide, soluble bromide, or two or more of these in the solutions, the ordinary method had to be modified somewhat. To the 20 c.c. of solution containing the hydrogen peroxide and other substances mixed as indicated below, 20 c.c. of 25 per cent. sulphuric acid were added and this mixture was then titrated with about N/10 potassium permanganate until a faint pink remained throughout the solution for a half minute. The pink gradually disappeared and was transformed to a tan color. If the titration was carried further a fairly permanent pink was finally obtained, but the results were not repeatable. By stopping each time at the first point the titrations could be checked to within 0.1 to 0.2 per cent. of each other and possibly closer.

This method of titration does not give directly the absolute concentration of hydrogen peroxide, owing to the action of the silver or silver sulphide sol, the gelatin, and the bromide on the permanganate. But since it is the percentage decomposition of the hydrogen peroxide in a given time, and not its absolute concentration which is desired, this was obtained by titrating first a sample immediately upon mixing, adding the 20 c.c. of 25 per cent. acid to the hydrogen peroxide before the latter was mixed with the other solutions. A second sample was mixed without the addition of the 20 c.c. of strong acid to the peroxide, and after an hour the 20 c.c. of acid were then added and the titration carried out as before. The percentage decomposition of the hydrogen peroxide was then easily calculated from the difference between these two titrations.

One very strict precaution had to be taken in all of this work, namely, to keep the hydrogen peroxide and the mixed solutions out of sunlight and even out of bright daylight, otherwise results could not be checked.

Decomposition of H_2O_2 in the Presence of Ag-gelatin or Ag_2S-gelatin Sol.—In each of several beakers 5 c.c. of silver sol and 5 c.c. of 1 per cent. gelatin were brought together. To each of these beakers were then added 10 c.c. of about 0.1 M hydrogen peroxide made acid or alkaline, with one exception, with a small measured quantity of normal acid or alkali. At the end of an hour these mixtures were titrated, in the order in which they were made up, with about N/10 acid potassium permanganate. A control series was titrated immediately upon mixing,[21] and from the data thus obtained, the percentage decomposition of hydrogen peroxide was determined. The pure hydrogen peroxide was also titrated before and after the experiment to be sure that its concentration did not change during the interim. The exact details of the analytical procedure are given above.

A similar series of measurements was made using silver sulphide sol in place of silver sol, and with about the same range of pH values. The pH values in each case were determined colorimetrically with dyed filter papers in comparison with a copy of Clark's color indicator chart.

The results of these measurements are summarized in Table I and Fig. 1.

It is seen that the activity of the Ag sol is greater than that of the Ag_2S at any given pH, and for the former was still as much as 0.49 per cent. at a pH as low as 2.4, whereas with the latter the decomposition became negligible at pH below 5.0.

Effect of the Presence of H^+ and Br^- Ions on the Decomposition of H_2O_2.—When a small quantity of potassium bromide was added to the mixture of gelatin, hydrogen peroxide and silver or silver sulphide sol, a somewhat different result was obtained with the latter, as can be seen in Table II and Fig. 1.

The amount of decomposition of hydrogen peroxide in an hour's time, where silver sulphide was added, was considerably higher in acid solutions than with Ag sol at the same pH, and was uniform over the whole range of pH values used up to

[21] In this case 20 c.c. of 25 per cent. H_2SO_4 were added to the H_2O_2 prior to adding the H_2O_2 to the remainder of the mixture, in order to minimize the error due to the catalytic decomposition of the H_2O_2 before and during the time of titration. The choice of one hour as the time of reaction was purely arbitrary, but was made long enough so that the errors of titration would not be large in comparison with the amount of decomposition in most cases.

TABLE I.

Decomposition of H_2O_2 in Presence of Ag or Ag_2S Sol. No Br^- Ions Present.

5 c.c. of 1 per cent. deashed gelatin, 5 c.c. of 0.02 per cent. Ag sol, 10 c.c. pure approximately 0.3 M H_2O_2 solution.									
No. of c.c. of N acid or alkali added		0.1 c.c. NaOH	0.01 c.c. NaOH	0	0.035 c.c. H_2SO_4	0.07 c.c. H_2SO_4	0.10 c.c. H_2SO_4	0.15 c.c. H_2SO_4	
Approximate pH resulting		8.8—9.2	6.2—6.6	5.2—5.6	4.4—4.8	3.8—4.2	3.2—3.6	2.2—2.6	Average
No. of c.c. of approx. N/10 $KMnO_4$ required	Immediately	16.50	.....	...	16.51	....	....	16.49	16.50
	After 1 hr.	7.16	14.24	16.07	16.31	16.34	16.35	16.42	
Percentage decomposition in 1 hr		56.6	13.7	2.61	1.16	0.97	0.91	0.49	

5 c.c. of H_2O_2, 5 c.c. 0.02 per cent. Ag_2S sol in 1 per cent. deashed gelatin sol, 10 c.c. pure approximately 0.3 M H_2O_2 solution.								
No. of c.c. of N acid or alkali added	0.07 c.c. NaOH	0.05 c.c. NaOH	0.02 c.c. NaOH	0	0.035 c.c. H_2SO_4	0.07 c.c. H_2SO_4	0.10 c.c. H_2SO_4	
Approximate pH resulting	6.0—6.4	5.4—5.8	4.8—5.2	4.0—4.4	3.4—3.8	2.4—2.8	1.8—2.2	Average
No. of c.c. of approx. N/10 $KMnO_4$ required — Immediately	16.52	.....	16.50	.....	.....	16.51	16.49	16.50
After 1 hr.	15.82	16.10	16.51	16.53	16.50	16.48	16.51	16.50 for pH below 4.8
	4.1	2.4	0	0	0	0	0	

TABLE II.

Decomposition of H_2O_2 in Presence of Ag or Ag_2S Sol and H^+ and Br^- Ions.

5 c.c. of 1 per cent. deashed gelatin sol, 5 c.c. of 0.02 per cent. Ag sol, 10 c.c. pure approximately 0.3 M H_2O_2 sol, 0.1 c.c. M KBr.									
No. of c.c. of N acid or alkali added		0.1 c.c. NaOH	0.01 c.c. NaOH	0	0.035 c.c. H_2SO_4	0.07 c.c. H_2SO_4	0.10 c.c. H_2SO_4	0.15 c.c. H_2SO_4	
Approximate pH resulting		8.8—9.2	6.2—6.6	5.2—5.6	4.4—4.8	3.8—4.2	3.2—3.6	2.2—2.6	Average
No. of c.c. of approx. N/10 $KMnO_4$ required	Immediately	16.50	16.51	16.48				16.50	16.50
	After 1 hr.	14.84	16.35	16.37	16.40	16.41	16.41	16.46	
Percentage decomposition in 1 hr		10.1	0.97	0.79	0.61	0.56	0.56	0.25	

5 c.c. of H_2O_2, 5 c.c. 0.02 per cent. Ag_2S sol, in 1 per cent. deashed gelatin solution, 10 c.c. pure approximately 0.3 M H_2O_2 sol, 0.1 c.c. M KBr.									
No. of c.c. of N acid or alkali added		0.15 c.c. NaOH	1.10 c.c. NaOH	0.07 c.c. NaOH	0.05 c.c. NaOH	0	0.035 c.c. H_2SO_4	0.10 c.c. H_2SO_4	
Approximate pH resulting		8.8—9.2	8.0—8.2	6.0—6.4	5.4—5.8	4.0—4.4	3.4—3.8	1.8—2.2	Average
No. of c.c. of approx. N/10 $KMnO_4$ required	Immediately	16.50	16.51	16.50	.....	16.51	.....	16.50	16.50
	After 1 hr.	12.11	13.23	15.41	15.42	15.40	15.41	15.41	15.41
Percentage decomposition in 1 hr		26.6	19.8	6.6	6.6	6.6	6.6	6.6	6.6

pH = 6.2, and then increased for higher values. When Ag was used, however, the amount of decomposition of H_2O_2 increased with increasing pH throughout the series, as before when no bromide ions were present, but throughout the series, the values with bromide were less than those without bromide at each hydrogen-ion concentration. Now, as noted below, the solution of silver sol in the presence of bromide ions is much more rapid than in their absence. This destruction of silver sol therefore explains why the degree of decomposition is less with bromide instead of greater, as one would expect if both silver sol and bromide ions were producing an effect on the decomposition simultaneously.

The Behavior of Commercial Hydrogen Peroxide.—The commercial hydrogen peroxide which we used in most of our previous latent fog and latent image intensification experiments had a pH value of from 1.4 to 3.0, depending upon its source. This acidity was due to the presence of sulphuric acid used as a preservative.[22] When added to a deashed gelatin solution with a pH of about 4.7 the pH of the commercial hydrogen peroxide was considerably raised. If a photographic plate, the gelatin of which has a pH value of about 5 to 6 when bathed in distilled water, is treated with acid hydrogen peroxide, the hydrogen-ion concentration of the solution is also very likely lowered somewhat (pH is raised), even though the gelatin in this case is not actually in solution. At any given acidity or alkalinity the behavior of commercial hydrogen peroxide in the presence of catalysts is not very different from that of the pure hydrogen peroxide. The former seems to be decomposed at a slightly lower rate than the latter at the same pH, possibly owing to the presence of certain organic preservatives, such as acetanilide.

It is seen from the above results that even under the complicated conditions existing in the photographic plate, decomposition of the H_2O_2 is greater in alkaline than in acid solutions. Clark's contention, therefore, requires careful consideration.

So far, we have considered only the decomposition of the H_2O_2 as affected by the catalysts under various conditions. Now let us turn to the effect of the H_2O_2 on the catalysts.

[22] This was tested by precipitation of $BaSO_4$ with $BaCl_2$ solution.

ACTION OF H_2O_2-GELATIN SOLUTION ON Ag SOL.

Deashed gelatin in the pure H_2O_2 solution (pH about 4.7) without addition of acid caused Ag sol to decolorize very slowly without change of hue, and to form a true solution of Ag^+ ions,[23] the anions probably being $(CO_3)^{--}$, since the solutions were not freed of CO_2 and were dilute enough not to form Ag_2CO_3 sol or to precipitate this substance. The presence of Ag^+ ions in the solution was indicated by the fact that a little KBr solution added to the mixture after loss of color caused a faint cloud of AgBr to form slowly. When the KBr solution was added at the time of mixing, there was an immediate change of color to lemon yellow, and a faint cloud of AgBr formed slowly. A trace of acid, or acid and KBr together, caused the same color change and the latter also the faint cloud. The Ag-gelatin sol-H_2O_2 mixture without acid had a pH of about 5.4 – 5.6. When acid (H_2SO_4) was added in increasing quantities to the original mixture of Ag, gelatin, and H_2O_2 without bromide, the loss of color became less and less marked, but in every case as the solutions were brought together the color changed from the reddish lubricating oil color of the colloid Ag through orange to lemon yellow, requiring usually several minutes to reach the latter color.

THE ACTION OF H_2O_2 ON Ag_2S IN THE PRESENCE OF ACID OR ALKALI AND SOLUBLE BROMIDE.

We have stated above that acid-H_2O_2 solution had no visible effect on Ag_2S sol. The same thing was apparently true when soluble bromide was also added. Yet Br_2 is supposed to be formed according to reaction (1) when H_2O_2 and acid and soluble bromide are brought together.

But Hickman, in this laboratory, has very recently shown [12] that when bromine water is added to a suspension of Ag_2S in water, even when added slowly and when Ag_2S is in excess, AgBr is formed quantitatively according to the equation,

$$Ag_2S + 4Br_2 + 4H_2O = 2AgBr + H_2SO_4 + 6HBr, \quad (4)$$

which expresses the net result of the reaction.

It is known, moreover, that when pure liquid bromine is

[23] After the above was written the investigation of A. Fodor on "The Solution of Silver Miscelles by Hydrogen Peroxide," *Koll. Zeits.*, **39**, 173–178 (1926), came to our attention.

added to dry Ag_2S there is a vigorous reaction with the formation of AgBr and S_2Br_2, and that S_2Br_2 is quickly hydrolyzed or oxidized by water to H_2SO_3 or H_2SO_4 and HBr.

Perhaps the acid H_2O_2 and bromide in our experiments above did give some bromine and this in turn reacted upon the Ag_2S sol, even though the effect was not visible; or perhaps with the low concentrations of the various substances used, especially of the H ions, the tendency to produce Br_2 according to reaction (1) was only very slight. The following experiments support the latter supposition.

Some pure Ag_2S washed free of soluble sulphates and sulphides was prepared. To about an equal amount of this in each of two test-tubes was added a dilute solution of KBr and acetic acid. To one of these was then added a little pure H_2O_2 solution and to the other an equal amount of water. The tubes were shaken for a couple of minutes and the contents filtered. On adding $BaCl_2$ solution to the filtrates they remained clear even on standing over night. The experiment was repeated, this time keeping the H_2O_2-acid-bromide solution in contact with the Ag_2S for about an hour. Again the $BaCl_2$ test showed no measurable amount of sulphate.

A third test was made, this time replacing the acetic acid with a solution of HCl somewhat more concentrated than that of the acetic acid and increasing the content of bromide. On adding the H_2O_2 to the solution in one of the tubes, it immediately became straw colored and on shaking a few minutes and filtering, the filtrate gave a positive test for sulphate, while the control tube remained clear.

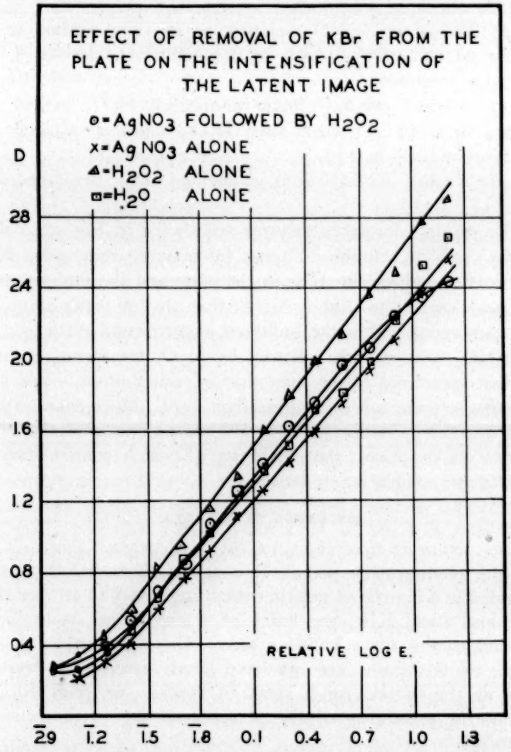
The experiment was now repeated using alkaline H_2O_2 with Ag_2S and soluble bromide. After shaking and filtering, the filtrate was made acid with dilute HCl, $BaBl_2$ solution was added, and then the H_2O_2 tube once more showed the presence of sulphate, and also some silver halide, since a part of the cloudiness was soluble in ammonia solution.

PREVENTION OF INTENSIFICATION OF THE LATENT IMAGE BY REMOVAL OF POTASSIUM BROMIDE FROM THE EMULSION.

As will be seen later, the presence of KBr in the plate is of the very greatest importance in connection with intensification of the latent image. In fact, the presence of some bromide ions

we believe to be essential, and we should expect their removal or partial removal to prevent or decrease, respectively, the intensification; this aside from any possible decrease in the rate of

FIG. 2.



decomposition of H_2O_2, due to its absence. The following preliminary experiment indicates that this is the case.

Four strips of Eastman Speedway plate were exposed behind a step tablet and were treated as follows:

(1) Bathed ten minutes in 0.005 per cent. $AgNO_3$ solution [24] made acid with H_2SO_4, to a pH of 2.5 – 3.0; washed twenty minutes in distilled H_2O, ten changes of two minutes each; bathed five minutes in 0.002 per cent. pure H_2O_2 solution; washed fifteen minutes in running water; developed, etc.

(2) Bathed in $AgNO_3$ solution as in (1); washed in ten changes of two minutes each in distilled H_2O; developed, etc. No H_2O_2 treatment.

(3) Washed one-half hour in distilled H_2O; bathed five minutes in 0.002 per cent. pure H_2O_2 solution; washed and developed, etc., as in (1).

(4) Washed one-half hour in distilled H_2O; developed, etc., as in (1).

The results of this experiment are shown in Fig. 2.

The $AgNO_3$ solution followed by washing removed a large portion if not all of the KBr in the plate and the intensification effect was lowered to slightly higher than that of water alone, the difference being within the limits of experimental error.

$AgNO_3$ solution not followed by H_2O_2 treatment produced an effect somewhat lower than that of water alone. We shall not attempt to explain this latter effect here. More exact experiments are being conducted along the above lines and also some experiments on plates, the emulsions of which contain varying amounts of soluble bromide.

DISCUSSION OF RESULTS.

The Action of Acid H_2O_2 on the Photographic Plate.—Consider the photographic plate. It contains silver halide crystals embedded in a matrix of gelatin containing also 5 to 10 per cent. water and some KBr, the latter of which is no doubt partly adsorbed to the silver halide grains. On or embedded in the surface of the grains are, we have good reason to believe, as stated at the outset, Ag_2S spots or specks—we omit for the moment the possibility of the presence of Ag in the sensitivity specks.

Although in a test-tube, in bulk, Ag_2S is attacked by bromine water to give AgBr, H_2SO_4 and HBr, Hickman has evidence

[24] It requires about five times this concentration of $AgNO_3$ acting for about the same length of time to produce intensification of the latent image.

which indicates that when the Ag_2S is isolated in the sensitivity specks in intimate contact with the silver bromide grains, and when light falls on and is absorbed by the grains, the reaction which possibly takes place with the very limited quantity of bromine set free by the photochemical decomposition

$$2AgBr + 2E = 2Ag + 2Br \qquad (5)$$

is the following:

$$2Ag_2S + 2Br = 4Ag + S_2Br_2. \qquad (6)$$

Hickman believes further that the S_2Br_2 in being oxidized by the moisture in the plate also causes the reduction of more silver bromide. He has discussed these and some other suggested intermediate reactions in his paper. Lambert and one of us [25] have investigated Hickman's hypothesis and found that, while certain suggested intermediate reactions are not admissible, the hypothesis as a whole is thermodynamically sound.

Hickman believes, and we do likewise, although there is at present no positive evidence to support it, that a smaller silver speck would be required than of Ag_2S to produce developability of a grain in a given developer under similar conditions; or if not that, at least that the rate at which development proceeds in the early stages from Ag specks is faster than from specks of Ag_2S.

When dilute acid H_2O_2 is first added to the plate, the local concentration of KBr in the plate is such that reaction (1) above very likely takes place with the formation of atomic or molecular bromine. It is reasonable to suppose that in the limited quantity formed, this would react with the Ag_2S of the speck according to equation (6), thus transforming at least part of it into Ag. It is also very likely that the acid H_2O_2 would convert part of this Ag, as well as of that already in the speck, into Ag ions, just as in the catalysis experiments above.

If all of the local supply of Br^- ions, that is, those in the immediate neighborhood of the speck, have not already reacted with the H_2O_2, they will no doubt pair off with their equivalent of these Ag^+ ions, thus forming some colloidal AgBr surrounded by an excess of Ag^+ ions. These particles being formed *in situ* and being embedded in gelatin will not diffuse away very readily, but will remain in close proximity to the specks on the compara-

[25] R. H. Lambert and E. P. Wightman, *J. Phys. Chem.*, **31**, 1249 (1927).

tively coarse grains. It is true that in the course of time, the bromide ions at a distance from the speck could and would no doubt diffuse in and alter these conditions, but the time would likely be long compared with that used in our experiments.

In this connection the following facts need to be considered:

(1) We have referred in our previous paper [1] to the already known fact that the sensitivity of a plate to light exposure can be increased by the addition of a small amount of $AgNO_3$ in solution to the grains, an amount sufficient to get rid of the trace of KBr present in the plate and probably to provide a few excess Ag^+ ions on the grains. We have also shown that an amount of $AgNO_3$ about equal to that producing increased sensitivity, but applied after exposure, will cause intensification of latent image on Speedway plates. We realize that from this experiment it is unsafe to generalize for all plates, but we at present have no reason to believe that other plates should behave very differently. Excess of Ag^+ ions on a grain, of course, make it spontaneously developable, simply because they are immediately reduced to metallic Ag by developer, and form specks of this of developable size.

It seems obvious that in order to be able to produce intensification of latent image as well as increased sensitivity without latent fog production, that the $AgNO_3$ must act in one of three ways, either (*a*) by merely reacting with the trace of KBr on the grains and thus leaving them "bare" of this protective agent, (*b*) by supplying very finely divided AgBr particles with a greater or less quantity of Ag^+ ions adsorbed to them, which as indicated in (2) and (3) below, are more easily developable than the comparatively coarse AgBr grains on the plate, or (*c*) by supplying, in addition, Ag^+ ions, to be *adsorbed to or very close to the sensitivity or latent image specks,* so that when developer reduces them the speck becomes increased sufficiently in size to make the whole grain developable.

(2) It is known that the solubility and surface energy of fine particles are greater than of coarse ones.[26] Dundon has also shown [27] that since fine and coarse particles of the same salt will

[26] G. A. Hulett, *Z. physik. Chem.*, **37**, 385 (1901); **47**, 357 (1904); M. L. Dundon and E. Mach, Jr., *J. Am. Chem. Soc.*, **45**, 2479 (1923).

[27] M. L. Dundon, *J. Am. Chem. Soc.*, **45**, 2658 (1923).

both come to a final equilibrium and exist together in contact with a saturated solution of the salt, that the "fine particles may have their solubility diminished by an electrical charge or adsorption effect on the surface."

This greater surface energy of the small particle with the electrical charge or adsorbed ions should increase its reducibility.

(3) Lottermoser has shown [28] that when AgI sol is formed in excess of K^+ and I^- ions the particles are negatively charged, and when formed in excess of Ag^+ and NO_3^- ions, they hold positive charges. It is, he found, much more difficult to remove adsorbed Ag^+ ions than I^- ions by washing, and the positively charged colloid miscelles are more unstable than are the negative. While a similar study has not yet been made of AgBr, its behavior and properties under similar circumstances ought to be quite similar to those of AgI.

From the above it would appear that whether acid H_2O_2, together with the soluble bromide in the plate, transforms Ag_2S specks, and perhaps some of the AgBr in immediate contact with it, into metallic Ag, into Ag^+ ions, into finely divided AgBr with adsorbed Ag^+ ions, or into mixtures of these; the developability of the grain should be increased by its action.

Dr. S. E. Sheppard has suggested to us that the $AgNO_3$ may work only when it is partly hydrolyzed. In the experiments described previously we washed the plates which had been treated with $AgNO_3$ solution with running tap water. This had a pH of around 5.0 to 5.5. It is known that at this pH the $AgNO_3$ is partly hydrolyzed and reacts with gelatin to form insoluble gelatinate. Hence the Ag cannot be completely washed out with water except on the acid side of the iso-electric point of gelatin. When developer is added to this Ag gelatinate, or whatever the complex may be, there is an immediate reduction to Ag.

ACTION OF ALKALINE H_2O_2 ON THE PHOTOGRAPHIC PLATE.

The above suggestions as to a possible mechanism apply only to the action of H_2O_2 in acid solution. In the case of alkaline H_2O_2 conditions are quite different. It is probable, as Dr. C. E. K. Mees has suggested to us, that, aside from a possible chemiluminescence or other effect of the catalytically decomposing

[28] A. Lottermoser, *Koll. Zeits.*, Zsigmondy Festschrift, **36**, 230 (1925).

H_2O_2, the alkaline H_2O_2 brings about a very slight development of the grain. That an exposed grain can be developed in *strongly* alkaline H_2O_2 has been known for a long time.[29]

The difficulty with this idea is that the fogging or intensifying effect should increase with increasing alkalinity whereas, as we have shown previously, the effect is in the opposite direction.

However, it is also possible that some AgOH is formed from the Ag_2S in alkaline H_2O_2, which AgOH, in developer, would undergo reduction to Ag.

It was noted above that some AgBr is formed when alkaline H_2O_2 acts on Ag_2S in the presence of soluble bromide. This AgBr, because of its formation in excess of the latter, would not be as easily developable even in alkaline solution as would AgBr formed in excess of Ag^+ ions.

As to the stages between distinctly acid and distinctly alkaline, *i.e.*, in the range of pH from 4.5 to 7, there must be a gradual lessening of the effect due to acid-H_2O_2-bromide and a gradual building up of the effect of alkaline-H_2O_2-bromide.

A thorough study of the action of H_2O_2 of various degrees of alkalinity on the sensitivity and latent image has never been made and is quite desirable.

It is evident that the above experiments, together with Hickman's theory of the rôle played by Ag_2S as a bromine absorber, furnish a basis for a purely chemical explanation of H_2O_2 action. At any rate it seems safe to say that Clark's contention that the effect is entirely chemical has at least some foundation. The work described here does not disprove the chemiluminescence theory although one fact, the increased rate of decomposition of H_2O_2 in alkaline solution, does cast doubt upon it. Our previous experiments revealing the fact that very little if any action of H_2O_2 occurs on an insensitive or desensitized plate to produce latent fog, and that only a slight intensifying effect is produced on the latent image on such a plate show that sensitizing nuclei are necessary, but do not distinguish between a chemical and a chemiluminescence view. Here, of course, the Ag_2S is either not present to any extent or has been largely removed before H_2O_2 treatment.

[29] M. Andresen, *Phot. Mittl.*, **28**, 296 (1891); "Eder's Jahrb.," 1893, p. 421; *Phot. Korr.*, **36**, 260 (1899).

SUMMARY.

(1) It has been shown that, just as with pure alkaline and acid solutions of hydrogen peroxide and a metal catalyst, alkaline hydrogen peroxide in the presence of gelatin-silver or gelatin-silver sulphide sol, with or without the presence of soluble bromide, is much more easily decomposed than acid hydrogen peroxide under similar conditions.

(2) It has also been shown that both acid and alkaline solutions of hydrogen peroxide in the presence of soluble bromide react with silver sulphide, in bulk, to give sulphuric acid or a sulphate and colloidal silver bromide.

(3) Colloidal silver was found to dissolve to a greater or less extent in gelatin-hydrogen peroxide solution with a pH of 5.5 or less, giving rise to silver ions which when soluble bromide is also present form colloidal silver bromide.

(4) These facts indicate that intensification of latent image, and probably also the effect of hydrogen peroxide on sensitivity or the production of latent fog, is chemical in nature as Clark has contended and that a chemiluminescence mechanism while it has not been disproved is not necessary in order to explain the phenomenon.

(5) A chemical mechanism is proposed based on Hickman's recent theory of the formation of latent image by light.

(6) It is proposed that the bromine set free by the action of acid peroxide on the soluble bromide in the plate being very limited in quantity acts on the silver sulphide speck to form metallic silver, which in turn may be partly converted by the acid hydrogen peroxide into silver ions, and if any soluble bromide is left in the vicinity some colloidal silver bromide is formed containing on its surfaces adsorbed silver ions. It is believed that any one or all of these, metallic silver, silver ions, or colloidal silver bromide with silver ions adsorbed, produces a greater degree of developability of the grain than the original silver sulphide speck.

(7) This view is supported by the experimental fact that if soluble bromide is largely removed from a plate by action of silver nitrate (less than an excess), hydrogen peroxide produces very little if any intensification of latent image.

Test for Zinc.—W. H. CONE and L. C. CADY, of the University of Idaho (*Jour. Am. Chem. Soc.*, 1927, **49**, 2214–2215), describe the following qualitative test for the presence of zinc. To the solution to be tested are added 5 drops of diphenylamine acetate solution (1 gram diphenylamine dissolved in 100 c.c. glacial acetic acid) and 5 c.c. of potassium ferricyanide solution (0.5 per cent. aqueous solution). If zinc be present, a dark brown, green, or purplish-black turbidity appears immediately. This test is more delicate than the cobalt zincate test for zinc, and may be used for the colorimetric estimation of the amount of zinc present. J. S. H.

The Extrusion of Bismuth Wire. D. C. STOCKBARGER. (*J. Opt. Soc. Am.*, May, 1927.)—A need for bismuth wire has arisen, especially in the construction of thermopiles where a combination of bismuth and silver is regarded as superior to copper-constantin. Since bismuth cannot be drawn into wire in the ordinary way, indirect methods have been resorted to. The Bulletin of the Bureau of Standards some years ago described a process in which the molten metal was poured from a height upon a smooth glass plate. The resulting thin sheet was rolled thinner and cut into strips.

This paper gives diagram and dimensions of a press for making circular bismuth wire by forcing the metal through an orifice .004 inch in diameter. The bismuth is in powdered form or in a slug, and the whole is heated to 100° C. Even at room temperature the wire can be forced through though a higher pressure is then necessary. "The bismuth wire is so pliable that it can be wound up on a spool as fast as it is formed. It can be wound around a ⅛-inch rod and straightened out again or bent several times in one place without breaking if care is exercised. It possesses good tensile strength." G. F. S.

Transmutation of Elements. A. SMITS. (*Nature*, Oct. 1, 1927.)—On May 1, 1926, *Nature* published a report on work done by Smits, which seemed to indicate the transmutation of lead into mercury. The results, it was stated, were hard to reproduce. The experiments have been continued and a careful search has been made for possible sources of contamination with mercury. With certain types of lamps traces of mercury were obtained while with others no evidence of mercury was found. When the greatest care was applied to have materials with no possible taint of mercury, no trace of this substance manifested itself. Professor Smits states: "At the moment I am, therefore, inclined to conclude that the mercury found in our earlier sparking experiments came, certainly partly and perhaps entirely, from the carbon disulphide." Thus evidence continues to accumulate that the controlled transmutation of elements of high atomic weight has not yet been accomplished. G. F. S.

A STUDY OF THE COMPRESSIVE STRENGTH DISPERSION OF MATERIALS WITH APPLICATIONS.

BY

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Pittsburgh, Penna.

INTRODUCTION.

THE dispersion of the ultimate strength of a material, especially pronounced in concrete, cast iron, and timber, has been shown to be an indispensable factor in the scientifically correct determination of a safe working stress for that material.[1] Aside from this utilitarian application and value, the investigation of the dispersion is of sufficient pure scientific interest in itself to warrant considerable study. The strength dispersions to which reference is made, are those variations from the mean exhibited in the ultimate strengths of individual test specimens made of a uniform material under uniform conditions, for which there are no assignable or controllable causes.

The purpose of the paper is to propound certain theoretical fundamental theorems for the compressive strength dispersion of homogeneous isotropic materials, and to substantiate these theorems, by previously published relevant data where available, and by specially prepared specimens where no data exist. The paper affords an opportunity in the analysis for an interesting application of the theory of sampling with small samples.

Basic experimental data from which the ultimate strength dispersion parameters may be computed are very meagre, since a large number of multiplicate test specimens is necessary to determine these parameters with a satisfactory degree of precision. To obtain the necessary data, Portland cement mortar and concrete were selected as the materials, and a number of test cylinders of these materials were made and tested in compression.

Variations in the mean strength of materials due to assignable and controllable causes, such as for concrete, variations in proportions, water content, etc., are not within the scope of the present paper. For a concrete produced under a definite set of fabricating conditions, the mean strength is a function of these variables, and can readily be determined by experiment upon a

[1] *Trans. Am. Soc. C. E.*, pp. 1126, 1132 *et al.*, **86**, 1923.

group of test specimens. The variations in strength dispersion which are studied in the present paper are those which result when fabrication conditions are constant, or as constant as practicable and efficient fabrication methods permit. To include the variations due to factors which can be eliminated tends to make the results of a statistical analysis less exact and of less value; it is very desirable, therefore, to eliminate all possible variables.

The beginning of the best known study of variations as made by Gauss included what is now known as the Theory of Errors, the errors being variations from a mean value due to unknown or unassignable causes. It is in the very essence of the problem that the causes of the variation be unknown or uncontrollable; if they are either known or controllable, then their effect may be directly calculated and not pursued through the mazes of statistical study.

A preliminary reconnaissance, such as the present investigation, cannot be both sufficiently comprehensive in scope and reasonably complete in detail. The experiments have been sufficient to check the theoretical forecast; yet unlimited investigation can be carried on upon the factors governing the statistical parameters of every material. The laws governing these parameters for concrete are complicated, and the parameters will vary with fineness modulus, grading, water content, etc.

APPRECIATION.

Through the courtesy of the Carnegie Institute of Technology, Pittsburgh, Penna., and the kind interest of Director Wm. E. Mott, of the College of Engineering, and Prof. F. M. McCullough, Head of the Department of Civil Engineering, permission was granted for the use of the materials, laboratory, and equipment, and the expense of the tests was borne by the Institute.

The writer is indebted to Messrs. W. A. Shewhart and Arne Fisher for their valuable suggestions on the statistical analysis.

THEORY AND APPLICATION.

Notation and Definitions.—The methods developed by Prof. Karl Pearson, which have been summarized by W. Palin Elderton in "Frequency Curves and Correlation," have been used in the analysis, with application of the corrections noted by Student [2]

[2] "Biometrika," see note below.

for samples when the number of individual observations or tests is small.

The usual form for σ, the mean error attributed to Bessel, is:

$$\sigma = \sqrt{\frac{\Sigma v^2}{n-1}}. \qquad (1)$$

In most statistical analyses the number of observations, n, is large and therefore the equation

$$\sigma = \sqrt{\frac{\Sigma v^2}{n}} \qquad (2)$$

has come into use. Student,[3] however, has shown that the distribution of σ is skew, and that the values of σ thus obtained from experimental data must be corrected, the smaller the sample, the larger the correction. Mr. Arne Fisher has called to the author's attention the method of Thiele and Andrae.

Andrae gives the formula:

$$\sigma = \sqrt{\frac{2\Sigma (x_u - x_v)^2}{n(n-1)}}. \qquad (3)$$

Where the $(x_u - x_v)$'s are the differences between the possible combinations taken two at a time and which may be formed from the n total observations in $\frac{n(n-1)}{2}$ ways.

The Thiele corrections involve the use of semi-invariants and complicate the computations without adequate return in the present application.

Student gives the correction factor

$$\sqrt{\frac{n}{n-2}}$$

to the formula (2).

Combining this we get

$$\sigma = \sqrt{\frac{\Sigma v^2}{n-2}} \qquad (4)$$

[3] "Biometrika," 6, 1908, p. 1, 11, 1917, p. 417. See also K. Pearson, "Biom.," 10, 1905, p. 522, and R. A. Fisher, "Biom.," 10, 1915, p. 507, and *Proc. Camb. Phil. Soc.*, 21, 1923, p. 655. The writer's attention was brought to this by Dr. W. A. Shewhart's paper, "Correction of Data for Errors of Averages," *Bell System Tech. Jour.*, Apr., 1926, 5, p. 308.

the form used throughout the present paper, credit being due to Doctor Shewhart for its suggested use.

v is the variation of the individual specimen from the mean value.

n is the number of specimens.

The Pearson parameters β_1, β_2 and κ have the usual significance.[4]

The shorter formula developed by C. A. F. Peters[5] may thus be written in the corrected form:

$$\sigma = \frac{\sqrt{\pi}\,\Sigma\,|v|}{\sqrt{2n\,(n-2)}} \qquad (5)$$

The values of σ tabulated in the paper have been computed by equation 4, because of its superior precision to equation 5.

The dispersion may be proportionately measured by the coefficient of variation Cv, given by the equation:

$$Cv = \frac{100\,\sigma}{m} \qquad (6)$$

where m is the mean value of the n variables.

Homogeneous and Heterogeneous Dispersion.—The parameter Cv measures dispersion. If the dispersion be the result of the free operation of one factor, then Cv will be invariable. If, however, the dispersion be the result of the irregular or irregularly restrained operation of that one factor, then the Cv as determined from experiment will vary in accord with the intensity of the operation of the factor during the interval when Cv was experimentally determined.

Concrete is a heterogeneous material, composed of aggregate varying enormously in size and shape. The strength of the concrete is a function of the mutual arrangement of these aggregates. If the various well-known factors which cause change in the strength of the concrete are kept constant, and the concrete in making is thoroughly mixed, then the variation in strength throughout the mass of the concrete will be solely due to the selection by chance of the mutual arrangement of the aggregate. The Cv will then be a measure of only one freely operating factor, therefore, a measure of uniform dispersion and constant

[4] See W. Palin Elderton, "Frequency Curves and Correlation."

[5] *Berliner Astronomische Nachrichten*, **44**, 1856, p. 29.

throughout the material. The Cv's calculated from several tests upon various poorly made batches, will not be equal. It is, therefore, desirable to separate the observations into several groups so that the dispersion may be known to be homogeneous or heterogeneous, by comparison of the Cv's computed from the several groups.

The strength dispersion of concrete has been found to be remarkably homogeneous, and in consequence of this and of the law enunciated in the next section frequency curves and parameters may be determined from a smaller group of test specimens than that required for the fields in which the previous statistical investigations in biology, etc., have been conducted.

Variation of Cv with Diameter for Compression Test Specimens.—A compression test cylinder of cross-sectional area a may be considered as composed of a units of area, each unit having a standard deviation (σ_0). Then by the extension and application of a well-known theorem in the theory of errors whereby the final probable error is equal to the square root of the sum of the squares of the probable errors, due to each individual operating cause, for a normal distribution we get:

$$\sigma_a = \sqrt{\Sigma (\sigma_0)^2} = \sqrt{a\sigma_0^2} = \sigma_0 \sqrt{a}. \tag{7}$$

Dividing by the mean value of the variable under consideration which would be ultimate load for σ_a and ultimate stress for σ_0, we get:

$$\frac{\sigma_a}{af_c'} = Cv_a \tag{8}$$

$$\frac{\sigma_0}{f_c'} = Cv_0, \tag{9}$$

where f_c' is the mean ultimate stress of the material.

From 7, 8 and 9 we get:

$$Cv_a = \frac{Cv_0}{\sqrt{a}}. \tag{10}$$

Cv_0 or unit coefficient of variation will be symbolized as cv; Cv_a will be written Cv. Cv and cv are connected by the equation:

$$cv = Cv\sqrt{a}. \tag{11}$$

Another constant of value is the coefficient of variation for

an element of area that will produce a strength of one thousand pounds, or one kip. Designating this by *kcv*, we get:

$$kcv = \sqrt{\frac{f_c'}{1000}} \cdot cv \cdot \tag{12}$$

We find from the foregoing that the standard deviation increases with the square root of the area; the coefficient of variation, *Cv*, decreases inversely as the square root of the area. The kip *cv* (*kcv*) and the unit *Cv* (*cv*) are constants for the material, and are independent of the diameter of the test specimen.

Arranging the results, and expressing the various constants each as functions of the other, we get:

Standard deviation,

$$\sigma = \sqrt{\frac{\Sigma v^2}{n-2}} \cdot \tag{13a}$$

Coefficient of variation,

$$Cv = \frac{100\,\sigma}{m} = \frac{100}{m}\sqrt{\frac{\Sigma v^2}{n-2}} \cdot \tag{13b}$$

Unit coefficient of variation,

$$cv = \frac{100\,\sigma}{m}\sqrt{a} = Cv\sqrt{a} = \frac{100\sqrt{a}}{m}\sqrt{\frac{\Sigma v^2}{n-2}} \cdot \tag{13c}$$

Kip coefficient of variation,

$$kcv = cv\sqrt{\frac{f_c'}{1000}} = Cv\sqrt{\frac{m}{1000}} = \sqrt{\frac{10}{m}}\,\sigma = \sqrt{\frac{10}{m}}\sqrt{\frac{\Sigma v^2}{n-2}} \cdot \tag{13d}$$

The safe stress (based on the normal curve) is given by the equation [6] which may be expressed in the form:

$$f_c = f_c' L_s \left(1 - \gamma \frac{\sigma}{f_c' a}\right) \tag{14a}$$

$$= f_c' L_s \left(1 - \gamma \frac{Cv}{100}\right) \tag{14b}$$

$$= f_c' L_s \left(1 - \frac{\gamma cv}{100\sqrt{a}}\right) \tag{14c}$$

[6] *Trans. Am. Soc. C. E.*, **86**, p. 1122, 1923.

$$= f_c' L_e \left(1 - \frac{\gamma k c v}{\sqrt{10 a f_c'}}\right) \qquad (14d)$$

L_e is the endurance limit of the material.

γ is a function of the safety desired. For one possibility in ten million, γ has been shown to be equal to 5.2.

f_c' is the mean ultimate compressive stress of the material as given in a column of cross-section area a.

f_c is the safe working stress.

Variation in Strength with Length for Columns.—The theoretical reduction in the strength of perfectly concentrically loaded columns due to increase in length, where failure occurs before buckling of the column, as in columns shorter than those for which Prof. R. F. Deimel's correction of Euler's column formula [7] criterion applies, may be considered as due to the greater length in which failure can occur.

If the length of the test cylinder from which a cv be calculated be taken as unity, then a column will be n units long and may be considered as composed of n individual units, each unit having the same strength dispersion as the test cylinders.

The column strength is then the strength of the *weakest* of the n individual units, and the average strength of a number of like columns would, therefore, be lower than the average strength of a number of cylinders.

If x_0 be the amount that the strength of the column of n units length is below the unit length column strength, then:

$$\left(\int_{-x_0}^{\infty} y dx\right)^n = \frac{1}{2} \quad \therefore \int_0^{x_0} y dx = \frac{1}{2} - \left(\frac{1}{2}\right)^{\frac{1}{n}};$$

for the normal curve,

$$\frac{1}{\sigma\sqrt{2\pi}} \int_0^{x_0} c^{-\frac{x^2}{2\sigma^2}} dx = 2\left[\left(\frac{1}{2}\right)^{\frac{1}{n}} - \frac{1}{2}\right] = P_t$$

n is known. Solve for P_t. From tables of P_t and t find t.

Then $x_0 = 1.413\ t\sigma$, where σ is determined from the unit length specimen.

The theory will apply only when the unit length is chosen so that failure of the specimen of unit length will occur in exactly the same manner as the failure of the short column. To illus-

[7] Stevens, "Indicator," **29**, No. 1, Jan., 1916.

trate, the failure of a short concrete column $\frac{l}{d} > K$ (where K is approximately 1.5), is by skew in a plane inclined at approximately 35° to the column axis. If the specimen have $\frac{l}{d} < K$, the least value where this failure may occur is in a plane inclined at more than this angle, the strength of the specimen is consequently increased and the foregoing theory invalidated.

It is not to be assumed that the foregoing theory completely explains the variation of strength with column length, below the valid minimum of the application of Euler's column formula. But one operating factor has been indicated. The variation of the modulus of elasticity over the column cross-section is, for example, another operating factor, as also the initial small departure of the column from the theoretical straight initial form.

Several groups of test data will illustrate the application of the foregoing theory. Attention is called to the agreement between theoretical and actual values for the groups having considerable difference in their Cv.

Tests of Concrete in Compression.

$\frac{L}{D}$	Relative Ultimate Column Strengths.		
	Actual.	Theoretical.	
2	100.0	100	$Cv = 5.71$ from group of 6 and same value from weighted Cv of all groups.
3.7	91.4	93.2	
8.0	90.3	90.6	
12.0	88.2	89.0	

C. Bach, *Deutsche Bauzeitung*, II, 1914, No. 5, p. 33.

Tests of Concrete in Compression.

$\frac{L}{D}$	Relative Ultimate Column Strengths.		
	From Representative Curve of Tests.	Theoretical.	
1.5	100	100	$Cv = 15.0$ computed from group of 55, 6 × 12″ cylinders, 1:5 and 1:3 mix. Cylinders in groups of 10; one group of 5.
2.0	97.5	97.0	
3.0	91.7	92.05	
4.0	88.3	89.1	

H. F. Gonnerman, Bull. 16, Structural Materials Research Laboratory, Lewis Institute.

Tests of Steel Columns.

	Test Results.	Compt. Results.	$C_P = 3.06$.
40	100	100	
80	98.4	96.8	

T. P. 328, National Bureau of Standards, from Table 15.

The theory just developed may be applied as a check upon the concentricity of the loading of short columns. It is to be noted that the theory is independent of, and is not to be taken as contradicting, the theory of the strength of shorter columns as developed by F. Engesser,[8] Th. V. Karman,[9] R. V. Southwell,[10] L. B. Tuckerman,[11] and others.

TEST RESULTS.

The original scope of the investigation was to include mortar compression specimens only, as it was presupposed that in order to obtain information of value, the number of multiplicate mortar specimens and of the usual size concrete specimens would be so large that the concrete series, by reason of its magnitude, would have to be undertaken as a separate investigation. The results obtained from the comparatively few small-size mortar specimens were so clear and impressive that some fifty-four concrete cylinders were included with results that corroborate those obtained from the small mortar cylinders.

The cylinders all had the length equal to twice the diameter. The diameters of the individual cylinders of the same nominal diameter were constant by a close approximation, and measured in inches were: 1.16, 1.98, 2.55, 3.84, 6.05, 8.16. Attention is called to the enormous difference between the smallest and largest specimen. The smallest weighed .2 lb., the largest 72 lbs. The sand or mortar specimens were made in the three smaller sizes, one batch including the 3.84-inch diameter, all made from the same sample of cement. The concrete specimens were made

[8] F. Engesser, *Zeitschrift f. Arch. u. Ing.-Wesen*, 1889, S. 455.

[9] Th. V. Karman, "Untersuchungen uber Knickfestigkeit, Mitteilungen uber Forschungsarbeiten auf dem gebeite des Ing.-Wesens," Heft 81, Berlin, 1910.

[10] R. V. Southwell, "The Strength of Struts," *Aircraft Engineering*, Jan. to May, 1920.

[11] L. B. Tuckerman, *Doctors' Dissertation*, Johns Hopkins University, 1921.

TABLE I.

Standard Sand Mortar Compression Cylinders. Test Data and Dispersion Parameters. Effect of Variation in Diameter.

Group Symbol.	Nominal* Diameter of Specimen. Inches.	Number of Specimens.	Mean Ultimate Load. Pounds.	Mean Ultimate Stress. Pounds per Square Inch.	Standard Deviation. σ	Coefficient of Variation. Cv	Unit Coef. of Variation. cv	Kip Coef. of Variation. kcv	Remarks.
M–1	2	6	10,470	3380	570	5.45	9.6	17.6	
M–2	1	6	2,550	2430	308	12.1	12.3	19.1	Ends of specimens concave, approx. $\frac{1}{32}$" in 2½" cylinder. Cylinders tested without capping.
	2	8	8,900	2870	740	8.3	14.7	25.0	
	2½	6	14,300	2800	1100	7.7	17.4	29.1	
M–3	1	6	3,050	2900	255	8.35	8.6	14.6	
	2	8	10,100	3260	670	6.65	11.6	21.1	Upper bearing defective: Not a plane surface. Specimens set in bearing at high speed.†
	2½	6	16,100	3160	1740	10.8	23.8	43.5	
M–4	1	6	3,100	2960	265	8.5	8.8	15.0	
	2	6	10,430	3370	730	7.0	12.2	22.4	
	2½	6	17,270	3390	830	4.8	10.9	20.0	
M–5	2	4	11,860	3830	650	5.45	9.7	18.9	
	1	4	4,420	4210	225	5.0	5.2	10.7	Tamped with 2-lb. iron rod.
M–6	1	6	3,780	3600	410	10.8	11.1	21.0	
	2	4	12,000	3870	885	7.3	13.0	24.8	

M–7	1	6	4,120	3930	330	8.1	8.3	16.4	
	2	7	11,600	3740	1210	10.5	18.4	35.4	Set in bearing block at high speed.†
	2½	6	16,750	3290	230	13.8	33.3	56.6	Set in bearing at very high speed.‡
M–8	1	4	5,960	5670	1040	17.4	17.9	42.5	Top of cylinder pressed firmly with trowel to force out excess water and make the top as strong as the rest of the cylinder.
	2	5	14,570	4700	1240	8.4	14.8	32.0	
	2½	6	20,611	4050	890	8.9	9.7	19.5	
M–*BS*	2	6	11,240	3620	825	7.3	12.9	24.5	
	2	5	12,000	3880	1070	8.9	15.6	30.8	
	2	6	11,930	3850	174	1.5	2.6	5.1	
	2	17	11,700	3780	665	5.15	10.0	19.5	Weighted mean of above three groups.
	2	17	11,700	3780	745	6.35	10.5	21.7	Seventeen as one group.

Data on tests: Cement: All one sample, well mixed.
Sand: Standard Ottawa silica.
Proportions: 1:3 by weight.
Water: 10.2 per cent. by weight.
Storage: In moist closet 20 to 24 hours, then in running water till test at 28 days.
Capping: Top end (as made) capped with plaster-of-Paris on day of test, except where noted.
Bearing: Spherical bearing block as lower bearing.
For 1" cylinders the testing head was lowered at testing speed in setting cylinders.
Other specimens set at next to lowest speed of testing machine, with reduced rheostat control.
All specimens rotated about longitudinal axis while being set in bearing.

* 1" Nominal Dia. = 1.157" mean.
2" Nominal Dia. = 1.985" mean.
2½" Nominal Dia. = 2.55" mean.

† Set at second highest speed.

‡ Set at highest speed, coasting. The initial load was less than 500 pounds; upper end of cylinders showed no visible signs of injury.

in the three larger sizes, from the same brand cement of approximately the same strength, but not the same sample as were the mortar cylinders. The specimens were all tested twenty-eight days after moulding. Mortar cylinders were placed in the damp

TABLE II.

Dispersion Parameters, Standard Sand Mortar Cylinders. Summary of Normal Results from Table I.

Group Symbol.	Nominal Diameter. Inches.	Number of Specimens.	Mean Ultimate Load. Pounds.	Mean Ultimate Stress. Pounds per Square Inch.	Standard Deviation. σ	Coefficient of Variation. C_v	Unit Coefficient of Variation. c_v	Kip Coefficient of Variation. k_{cv}
M–3	1	6	3,050	2900	227	7.45	7.6	13.0
M–4	1	6	3,110	2960	236	7.6	7.8	13.4
M–6	1	6	3,780	3600	364	9.6	9.8	18.7
M–7	1	6	4,120	3930	296	7.2	7.4	14.6
Mean		24			281	7.96	8.16	14.9
M–1	2	6	10,470	3380	507	4.9	8.6	15.7
M–4	2	6	10,430	3370	649	6.2	10.9	20.0
M–5	2	4	11,860	3830	528	4.5	7.9	15.4
M–6	2	4	11,990	3870	719	6.0	10.6	20.2
M–*BS*	2	17	11,700	3780	586	5.1	8.9	17.2
Mean		37			592	5.23	9.2	17.5
M–4	2½	6	17,270	3390	741	4.3	9.7	17.8
M–8	2½	6	20,610	4050	792	3.8	8.7	17.4
Mean		12			767	4.06	9.2	17.6
Mean of 3 means weighted		73					8.9	16.7

closet from 20 to 24 hours, then in running water, and capped with plaster-of-Paris on the top end (as moulded) on the day of testing. The concrete cylinders were sprinkled, capped with a 1 : 1 mortar finished to a true surface, and at 48 hours placed in running water.

The temperature of the laboratory and the water varied

TABLE III.

Mortar and Concrete Test Cylinders. Variation in Diameter and Aggregate. Mortar Cylinder Test Data.

Group Number.	Proportions By Weight.	Proportions By Volume.	Mixing Water. Per Cent.	Consistency.*	Ultimate Cylinder Load, Pounds. Cylinder Diameter, Inches. 1.157	1.985	2.55	3.84
					7510	18,840	28,530	
					6880	19,030	28,850	
Chi	1:3	1:2.6	10.2	.95	7370	17,900	28,000	
					6930	19,120	29,170	
					6510	19,070	29,770	
					7185	19,540		
Mean Ultimate Load					7060	18,920	28,860	
Mean Ultimate Stress					6710	6,110	5,660	
					4020	10,240	14,980	
					3900	10,560	15,140	
NYD	1:3		10.45	.95	3860	10,780	14,800	
					4560	10,660	16,310	
					3370	9,190	15,350	
					4020	10,070	14,460	
Mean Ultimate Load					3955	10,250	15,170	
Mean Ultimate Stress					3760	3,310	2,970	
					2980	9,090	14,900	34,110
					2800	8,990	15,180	35,120
					3240	9,910	15,810	34,200
					3890	9,040	15,850	34,670
NYW	1:3		13.2	1.20	3390	10,380	15,700	37,130
					3700	8,830	15,190	35,830
					3440	9,150	13,080	35,700
					3850	8,990	15,230	
					3300	8,930	14,700	
						8,770		
Mean Ultimate Load					3400	9,210	15,070	35,250
Mean Ultimate Stress					3230	2,970	2,960	3,030

*Definition of Prof. Duff A. Abrams, Bull. No. 1, Structural Materials Research Laboratory, Lewis Institute, Chicago.

TABLE III—*Continued.*

Concrete Cylinder Test Data.

Group Number.	Proportions. By Volume.	Mixing Water. Per Cent.	Consistency* and Slump.	3.84" Dia.		6.05" Dia.		8.15" Dia.	
				Ultimate Load, Pounds.	Density, Pounds per Cubic Foot.	Ultimate Load, Pounds.	Density, Pounds per Cubic Foot.	Ultimate Load, Pounds.	Density, Pounds per Cubic Foot.
					†	80,170	†		†
						86,260			
L-1	1:2:4	6.75	.9	36,220		82,440		137,150	147.6
			Zero	37,210		76,550		144,210	148.8
			Slump	30,320		86,560		143,200	147.4
				33,100		89,140		146,050	148.4
Mean				34,210	149.5	83,520	150.3	142,650	148.1
Mean Ultimate Stress				2,950		2,900		2,730	
				35,310	150.0	80,490	148.7	141,520	147.0
				32,790	150.0	70,150	148.7	151,220	147.7
L-2	1:2:4	6.75	.9	37,600	150.0	78,760	148.4	134,280	146.6
			Zero	38,900	151.0	82,890	149.8	149,070	147.6
			Slump	31,570	151.0	77,100	150.3	140,400	148.8
				33,170	151.0	81,000	148.7	133,330	146.9
Mean				34,890	150.5	78,360	149.1	141,640	147.3
Mean Ultimate Stress				3,005		2,710		2,710	
Mean Density at 28 Days					152.0		152.0		149.0
				17,620	148.0	60,550	146.0	101,130	145.5
				14,740	148.0	55,330	147.6	114,490	146.1
L-3	1:2:4	9.43	1.27	18,940	148.0	55,510	148.0	112,000	146.1
			6"	16,330	147.0	53,500	147.0	101,400	144.9
			Slump	19,260	147.0	50,730	147.0	103,570	145.1
				19,220	148.0	49,930	147.0	106,440	145.8
Mean				17,685	147.7	54,260	147.1	106,505	145.6
Mean Ultimate Stress				1,520		1,880		2,040	
Mean Density at 28 Days					149.2		148.5		146.3

*Definition of Prof. Duff A. Abrams, Bull. No. 1, Structural Materials Research Laboratory, Lewis Institute, Chicago.

†After 48 hours.

considerably, due to the changing season of the year over which the experimental work was spread. This temperature variation caused a strength variation. Although for the standard sand mortar cylinders direct comparison can be made only between the strengths of the various diameter specimens made at the same time, the end-results obtained by averaging the values of the dispersion parameters are almost as satisfactory as if the temperature had remained constant and in consequence the ultimate strength had not varied.

TABLE IV.

Grading of Sands and Gravels in Mortar and Concrete Cylinders.

Sieve.	Standard Ottawa Sand.	N. Y. (Cow Bay) Sand.	Chi. (Torpedo) Sand.	*L*-1 and 2 Gravel.	*L*-3 Gravel.	Allegheny Sand. Used in *L*-1, 2 and 3.	
100	100	98.3	99.5	100	100	97.8	
50	100	89.9	94.4	100	100	78.4	
30	96.7	56.0	67.3	100	100	39.6	
16	0	29.3	44.7	100	100	20.5	
8	0	12.5	27.9	100	100	9.4	
4	0	2.8	8.4	99.5	97.3	0.3	
⅜″	0	0	0	98.0	93.3	0	
¾″	0	0	0	86.2	75.2	0	
1″*	0	0	0	55.7	49.0	0	*Not included in computing fineness modulus.
1¼″*	0	0	0	0	25.0	0	
1½″	0	0	0	0	2.5	0	
Fineness modulus.	2.97	2.89	3.42	7.84	7.66	2.46	

Fineness Modulus Concrete Aggregate (Sand and Gravel): *L*-1 and 2 = 6.21; *L*-3, 6.07.

The tabulated and computed results of the tests are given in Tables I to VI and Figs. 1 to 8. Since no information of value is to be gained from the direct test loads of each individual specimen of the group, these have been given only for the groups other than made of the standard sand.

It would not be feasible in an introductory investigation, such

TABLE V.

Dispersion Parameters. Mortar and Concrete Compression Cylinders. Variation in Aggregate and Diameter.

Group Symbol.	Nominal† Cylinder Diameter. Inches.	Number of Specimens.	Mean Ultimate Load. Pounds.	Mean Ultimate Stress. Pounds per Square Inch.	Standard Deviation. σ	Coefficient of Variation. C_v	Unit Coefficient of Variation. c_v	Kip Coefficient of Variation. k_{cv}
M Group excluding abnormal specimens.	1	24		3800*	280	8.0	8.2	14.9
	2	37		3800*	590	5.2	9.2	17.5
	2½	12		3800*	770	4.1	8.9	16.7
Mean		73		3800*				
Chi	1	6	7,060	6720	410	5.8	5.9	15.4
	2	6	18,920	6110	610	3.25	5.7	14.1
	2½	5	28,900	5660	770	2.65	6.0	14.3
Mean		17					5.9	14.7
NYD	1	6	3,960	3760	430	10.9	11.0	21.3
	2	6	10,250	3310	650	6.4	11.2	20.4
	2½	6	15 170	2980	710	4.7	10.7	18.4
Mean		18					11.0	20.0
NYW	1	9	3,400	3230	400	11.7	12.3	22.2
	2	10	9,210	2970	550	6.0	10.5	18.2
	2½	9	15,070	2960	910	6.0	13.5	23.2
	4	7	35,250	3030	1170	3.3	11.3	19.7
Mean		35		3050			11.9	20.8
L–1	4	4	34,200	2950	3840	11.2	38.2	65.7
	6	6	83,500	2900	5230	6.3	33.6	57.3
	8	4	142,600	2730	4730	3.3	24.0	39.5
L–2	4	6	34,900	3000	3250	9.3	32.0	55.5
	6	6	78,400	2710	5060	6.5	35.0	57.0
	8	6	141,600	2710	8250	5.8	42.0	69.2
Mean of *L*–1 & *L*–2	4	10					34.2	59.6
	6	12					34.1	57.2
	8	10					34.8	57.3
		32		2840			34.3	58.0
L–3	4	6	17,700	1520	2060	11.7	40.0	49.0
	6	6	54,300	1880	4310	8.0	43.0	58.3
	8	6	106,500	2040	6300	5.9	43.0	61.0
Mean		18		1810			41.0	56.0

*Approximate stress that would develop under curing temperature conditions identical with other cylinders.

†Actual Diameters: 1.157 3.84
1.985 6.05
2.55 8.15

as the present, to attempt to obtain the correlation between the unit coefficient of variation (cv) and the other variables of a concrete: Fineness modulus or grading, water content, various cements, ages of test specimens, etc., and this has not been attempted. In a general way, it is clearly shown that the largest size of the aggregate greatly affects the cv, but much more

TABLE VI.

Summary of Mortar and Concrete Dispersion Parameters with Their Precision Measure.‡

Group Symbol.	Number of Cylinders.	Maximum Size of Aggregate. Inches.*	Unit Coefficient of Variation. cv	Kip Coefficient of Variation. kcv	k $(\beta_1 = k^2)$	β_1	β_2	κ†
M–BS	17	.04	10.5±1.0	21.7	.6 ±.6	.30 ±.65	3.65±1.19	+.6
NYD	18	.125	11.0±1.05	20.0	.1 ±.6	.006±.09	2.91±1.15	−.02
NYW	35	.125	12.2± .7	20.8	.1 ±.4	.016±.11	3.43± .83	+.02
Chi	17	.20	5.85±.6	14.7	0 ±.6	.001±.04	2.37±1.19	0
L–1	14	1.00	32.5±1.1	54.7	.4 ±.6	.14 ±.50	1.81±1.71	−.05
L–2	18	1.00	36.2±1.1	60.6	.2 ±.6	.024±.18	1.56±1.15	−.01
L–3	18	1.25	41.5±1.25	56.0	.1 ±.6	.019±.16	1.96±1.15	−.005
L–1, 2 and 3	50				0 ±.17	0±0	1.96± .69	0
Group of 137	137				.24±.21	.06 ±.10	2.63± .42	−.05

* Size of largest screen upon which 10 per cent. or more of aggregate is retained.

† These values are without significance because of the values and standard deviations of β_1. The 50 per cent. probability range will cause huge variations in κ. κ is undoubtedly very close to zero, and probably zero in each case.

‡ Expressed as a standard deviation, not a probable error.

experimental data must be obtained before information on this point of structural design value is obtained.

The groups irregularly made or tested were partly the outcome of design and partly of necessity, where very limited time at the operator's disposal forced the testing hurriedly or under unusual conditions. Were the unit cv constant for all tests, there would be the possibility that this cv was a function of the testing machine rather than of the material or of the test specimens. The great variation in cv caused by the unusual or

incorrect testing practically eliminates the possibility of the *cv* being a function of the testing machines.

Of importance in the testing of specimens, the *cv* may be used to great advantage in the checking of the methods of fabrication

TABLE VII.

Dispersion Parameters for Concrete. Variation with Age.

Type of Aggregate.	Age. Weeks.	Number of Specimens.	Mixing Water. Per Cent.	Ultimate Stress. Pounds per Square Inch.	Standard Deviation of Ultimate Stress. σ	Coefficient of Variation. Cv	Unit Coefficient of Variation. cv	Kip Coefficient of Variation. kcv
Granite	4	12	8.3	3050	270	8.8	62	110
	52	9	8.3	5270	350	6.6	47	108
	52	12	8.1	5310	390	7.3	52	119
Mean								
Limestone	4	21	10.0	2490	360	14.3	100	160
	13	18	10.0	3630	300	8.4	59	113
	26	19	10.0	3800	180	4.7	33	65
	52	18	10.0	4370	310	7.2	51	107
Mean								
Gravel	4	6	9.4	3260	410	12.6	89	160
	52	9	9.4	5280	470	9.0	64	147
Mean								
Cinders	4	15	18.9	1660	150	9.1	64	82
	13	14	18.9	2220	110	5.0	36	53
	26	15	18.9	2520	170	6.9	49	77
	52	19	18.9	2760	135	5.0	35	58
Mean								

Tests of 8-inch diameter cylinders.
Source: Technologic Paper No. 2, National Bureau of Standards.

or of testing. The *cv* gives a far more accurate measure of the deviation of the testing or fabrication conditions of a group from the normal conditions than does the mean ultimate strength. From Table I it can be seen that the change in strength due to

TABLE VIII.

Safe Stresses for Concrete. Affect of Maximum Aggregate Size and Diameter of Column.

Column Data.	Maximum Size of Aggregate. Inches.	Safe Stresses Based on a Unit *cv* of 30 for a One-inch Maximum Aggregate. In Terms of Ultimate Stress.	Safe Stresses Based on a Unit *cv* of 30 for a One-inch Maximum Aggregate. Pounds per Square Inch.	Safe Stresses Based on a Unit *cv* of 60 for a One-inch Maximum Aggregate. In Terms of Ultimate Stress.	Safe Stresses Based on a Unit *cv* of 60 for a One-inch Maximum Aggregate. Pounds per Square Inch.
62" core diameter	¼	.493	1360	.485	1340
Selected from practice. Used as a cap for concrete piers varying from 35 to 40 feet in length. Cap proper 4 feet long, 66 in. outside diameter. Spiral: 62" dia., 3" pitch, ½" dia. wire. Rods: One in. sq. spaced 6" around spiral circumf. Ratio of Reinforcement: Spiral .004 Rod .010 1:2:4 Concrete. Design Stress 500 lb. per sq. in. Ultimate assumed as 2000, or 2760 as reinforced	1	.485	1340	.476	1310
	2	.476	1310	.442	1220
	3	.456	1260	.413	1140
	4	.442	1220	.385	1062
	6	.413	1140	.327	902
	12	.327	902	.154	425
	24	.154	425	0	0
12" core diameter	½	.463	1280	.426	1175
The same concrete and reinforcement ratio as 62" column above.	¾	.445	1230	.390	1075
	1	.426	1175	.354	977
	1½	.390	1075	.280	770
	2	.354	977	.205	565
	3	.280	770	.059	155
	4	.205	565	0	0
	5	.132	364	0	0
	6	.059	155	0	0
	8	0	0	0	0

Maximum Aggregate Size.	Safe Stresses for 2760 Pound per Square Inch Concrete (2000 Pound per Square Inch without Reinforcement). Based on a Unit *cv* of 30 for One-inch Maximum Aggregate. Column Diameter, Inches.							Based on a Unit *cv* of 60 for One-inch Maximum Aggregate. Column Diameter, Inches.						
Inches.	8	12	18	24	36	48	60	8	12	18	24	36	48	60
¾	1160	1230	1270	1300	1325	1340	1350	925	1076	1086	1230	1260	1300	1320
1½	925	1076	1086	1230	1270	1300	1310	470	770	830	1076	1086	1230	1260
3	470	770	830	1076	1086	1230	1255	0	155	580	770	990	1105	1136
6	0	155	580	770	990	1105	1138	0	0	0	166	568	773	895

temperature difference is almost equal to the change in strength due to the unusual condition of tamping the specimen with an iron rod; yet, for differences of temperature, the *cv* varied but slightly, apparently not a function of the temperature, while the unusual condition of tamping caused a large variation in the *cv*. Again, those specimens with concave ends, uncapped, show an average *cv* 50 per cent. greater than the average of the normal specimens, while the average ultimate strengths are not more than

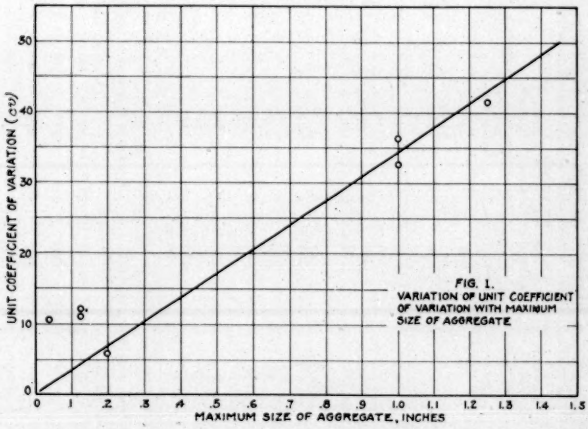


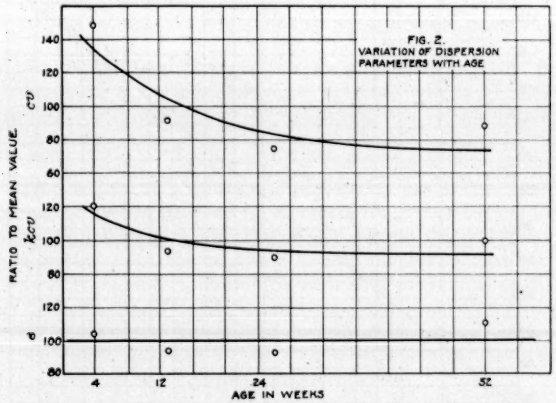
FIG. 1.
VARIATION OF UNIT COEFFICIENT OF VARIATION WITH MAXIMUM SIZE OF AGGREGATE

10 per cent., probably less, below the normal. For those specimens (Group *M*–8) with the top pressed while making, the variation from the average normal *cv* was 65 and 45 per cent., while the strength variation was not more than 45 and 15 per cent., respectively.

The test results emphasize the extreme care necessary in setting the compression specimens in the testing machine. Increase in dispersion resulted from running the upper platten, in setting, at the next to lowest speed of the machine, even though the cylinder could be rotated by hand about its longitudinal axis after it had been fixed by the upper platten. To obtain the best results, the cylinders, especially the smaller sizes, were set with the head running at the lowest possible gear speed, but

with rheostat control set for higher speed than for application of load.

Coefficient of Variation a Function of the Diameter.—The range covered by the tests was wide, mortar and concrete aggregates varying from well-graded (Chicago sand) to poor-graded (Ottawa Standard) mixtures from very dry to very wet, the specimens varying greatly in size and in size of largest aggregate. The variation in diameter was large enough sufficiently



to influence the dispersion, for the specimens in the *NYW* Group varying with a range of 3 to 1, certainly sufficient to cause a noticeable variation in the cv, if existing.

The unit coefficient of variation for all groups was calculated from equation 11,

$$cv = Cv\sqrt{a}.$$

The check upon this equation, from groups of tests of specimens of varied diameters, is a constant value for cv, independent of the diameter. As can be seen from every group of normally tested mortar and concrete specimens, the cv is constant, or as constant as test conditions and statistical inference warrant.

The analysis as one group of the test results of the cylinders of varied diameter made of one material (as shown in Figs. 3

to 6), serves to corroborate the theory of the variation of the dispersion with the diameter, as well as to establish the form of the frequency curve. In the analysis of groups of cylinders of several diameters as one group, the individual variations from the group mean were multiplied by the square root of the

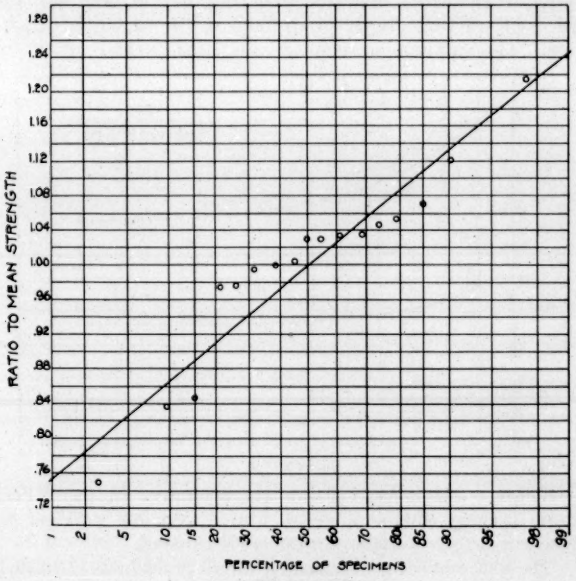


FIGURE NO 3

TOTAL FREQUENCY CURVE OF 17 MBS CYLINDERS

$\sigma = 10.5 \pm 1.0$
$\beta = .30 \pm .65$
$\beta_2 = 3.65 \pm 1.2$
$K = .6$ (Not significant).

cylinder area to obtain a reduced variation, an operation permissible by reason of equation 11. As a corollary if the reduced variations, therefore, conform to a definite form of curve, the law given by equation 11 must hold.

By reason of the method of treating the individual variations

from the mean, the coefficient of variation of the groups should be the unit coefficient of variation of the material. The values thus obtained agree with the values calculated from the individual groups of approximately six specimens.

The determination of the precision of the parameters computed from the whole group of specimens of one material is of interest. The standard deviation of $k-\beta_1$ is $\sqrt{\frac{6}{n}}$ and of β_2 is $\sqrt{\frac{24}{n}}$, where n is the number of individual observations. In the present case, however, for the computation of the precision of cv, n must be taken as the total number of square inches in the cross-sections of the whole number of cylinders in the group.

Thus, although moments of the fourth degree are necessary to compute Pearson's constants, and Charlier has warned against the use of greater than second moments for groups of less than 1000, the results give information far beyond the reliability to be expected from the relatively minute number of specimens.

Continuing and extending the method of combining the number of specimens of varied diameter but of one material, the whole group of 137 cylinders and of several materials was analyzed as one group, shown in Fig. 8. To accomplish this, the individual variations were treated by the equation

$$v = \frac{10\, v_0}{mCv}, \qquad (15)$$

where v_0 is the original variation from the mean of the group;
v is the corrected variation, as plotted in Fig. 8;
m is the mean value of the group of one diameter and material to which the variation v_0 belongs;
Cv is the coefficient of variation for the whole group just mentioned.

The analysis clearly indicates without question that the strength frequency curve is symmetrical. The mortar specimens and the whole group of 137 strongly indicate the normal (Pearson's Type VII) form:

$$y = \frac{1}{\sigma\sqrt{2\pi}} C^{-\frac{x^2}{2\sigma^2}}. \qquad (16)$$

There is an indication that for concrete the curve is of the symmetrical form with limits (Pearson's Type II). The difference from the normal type is not marked, however, and for engineering calculations the normal form may be safety assumed.

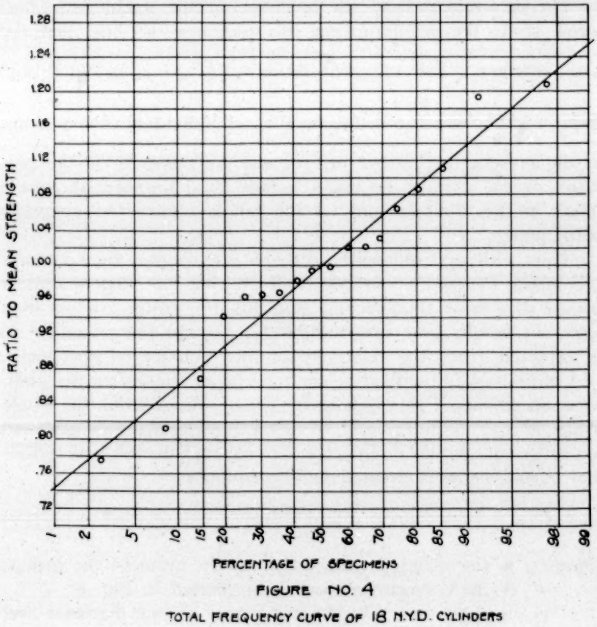


FIGURE NO. 4

TOTAL FREQUENCY CURVE OF 18 N.Y.D. CYLINDERS

$\sigma = 11.0 \pm 1.05$
$\beta_1 = .006 \pm .09$
$\beta_2 = 2.91 \pm 1.2$
$K = .02$

Moreover, the total frequency curve as plotted (Fig. 8) strongly indicates the normal type for the lower branch.

Variation of Coefficients of Variation with Maximum Size Aggregate.—By no means sufficient data were gotten to accurately obtain the relation between the *cv* and the size of largest aggregate. The values that were obtained, however, are posi-

tive proof that some relation, however crude, must exist, as is clearly indicated by the plotted values given in Fig. 1. It is to be expected that the *cv* is a function not only of the maximum size aggregate, but of the grading (as indicated by Prof. Duff

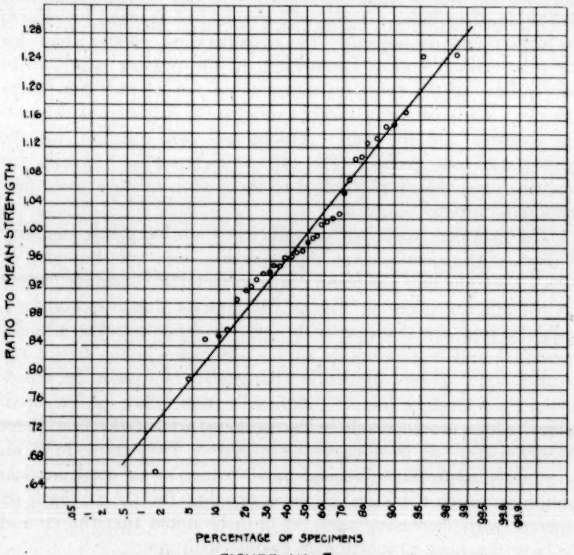


FIGURE NO. 5

TOTAL FREQUENCY CURVE OF 35 NYW CYLINDERS

$\sigma = 12.2 \pm .7$

$\beta_1 = .02 \pm .11$

$\beta_2 = 3.43 \pm .83$

$K = +.02$

Abrams' Fineness Modulus [12] or some other method), ratio of largest size aggregate to test cylinder diameter, water content, etc. Such relationship can only be determined by a very large number of tests. From the concrete tests it would appear

[12] Bulletin No. 1, Structural Materials Research Laboratory, Lewis Institute, Chicago.

that for a given mix the *kcv* is constant and independent of the water content.

Change in the Dispersion Constants with Age.—The chosen source of data is *Technological Paper No. 2*, U. S. Bureau of Standards. This experimental work was performed before the technique of cylinder making and testing had reached its present perfection and consequently the dispersion is greater than for the other concrete tests enumerated in the present paper. For two causes, all the cylinders tested could not be included in the analysis: Many of the cylinders exceeded the capacity of the testing machine and the water content was not constant for the cylinders of one group. The cylinders chosen as a group for analysis were, therefore, limited to those with but one fixed percentage of mixing water.

The cylinders were not of sufficiently uniform heterogeneity to disclose the exact change of dispersion with age, but give at least an insight into the trend. The dispersion constants plotted against age are given in Fig. 2. It appears that σ is constant, while *Cv* and *kcv* decrease with age. A representative straight line for σ and representative curves are given in the figure for *cv* and *kcv*. These dispersion characteristics cannot be represented by a straight line of unlimited extent, since for negative values, which would result in the prolongation of the line, these characteristics are imaginary and absurd. They must have an asymptotic approach to some fixed value, or a mathematical minimum, much the same as the maximum for the strength of concrete with increasing age. It is to be noted that the *cv* and *Cv* have the same proportionate change with age.

Application of the Results to the Determination of Safe Stresses for Concrete.—It has been shown [13] that the safe working stress, in compression may be expressed by an equation (14*a*, 14*b*, 14*c*, 14*d*) in the form:

$$f_c = L_c f_c' [1 - \gamma [\phi (v)]] \qquad (17)$$

in which f_c is the safe working stress;

f_c' is the mean test cylinder stress;

$\varphi(v)$ is a function of one of the frequency curve parameters.

It is to be noted that for concrete, the equation gives a safe stress at the definite age at which the test cylinders determining

[13] *Trans. Am. Soc. C. E.*, **86**, p. 1122 *et al.*, 1923.

f_c' are tested. For concrete L_ϵ is approximately .5. For γ the value of 5.2 may be used.

If σ for concrete remain constant with increase in age, as is indicated by test results, then it is readily seen that the increase in working stress with age is approximately equal to one-half of the concomitant increase in ultimate strength; that is, if a

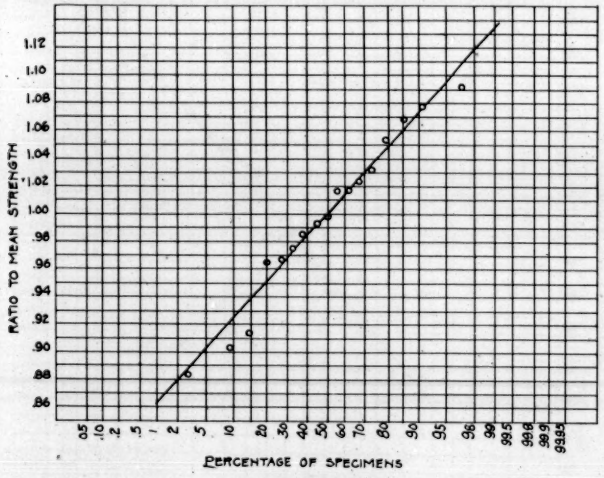


FIGURE NO. 6

TOTAL FREQUENCY CURVE OF THE GROUP OF 17 Chi CYLINDERS.

σ = 5.85 ± .6

β_1 = .001 ± .04

β_2 = 2.37 ± 1.2

K = 0

2000 pound per square inch concrete at twenty-eight days have a 500 pound per square inch safe stress (25 per cent. of ultimate), and if the ultimate strength at one year be 4000 pounds per square inch, then the safe stress will be 1500 pounds per square inch or 37½ per cent. of the ultimate strength.

To illustrate the influence of the variation of maximum size of aggregate and of column diameter upon safe working stresses,

Table VIII is given. The safe stress calculations for the table are based upon the tentative straight-line relation given in Fig. 1. The stresses in the table are based upon two unit coefficients of variation. It is not to be expected that commercial concrete will

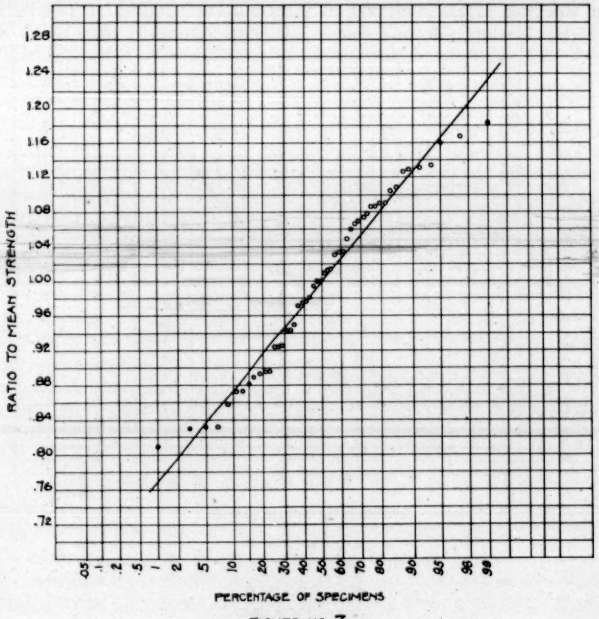


FIGURE NO. 7

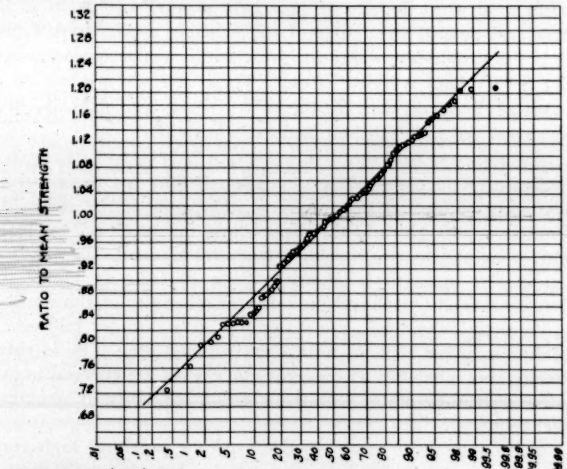
TOTAL FREQUENCY CURVE OF 50 CONCRETE CYLINDERS
GROUPS L-1, L-2, L-3.

$\sigma = 10.01 \pm .9$
$\beta = 0 \pm 0$
$\delta_1 = 1.96 \pm .69$
$K = 0$

have a coefficient less than 30 for a one-inch aggregate, nor is it reasonable to suppose that the value will be greater than 60, and the safe stresses have been computed and given in the table based on each of these two values.

The table forcefully illustrates the influence of aggregate size

upon safe stresses. For the large concrete column it can be seen that there is within reason practically no upper limit to the maximum size of aggregate that may be used, head size boulders giving 66 per cent. of the magnitude of the stress to be obtained by using the smallest practical size—½ inch. There is, however,



NOTE: BETWEEN 10 & 90 % THE OBSERVED POINTS ARE SO CLOSE THAT THEY CANNOT ALL BE GIVEN IN THE FIGURE.

FIGURE NO. 8

TOTAL FREQUENCY CURVE OF 137 MORTAR & CONCRETE CYLINDERS.

Composed of the Sub-groups:
17 MBS 18 NYD
17 Chi 32 L-1 & L 2
35 NYW 18 L-3

$\delta = 9.89 \pm 0.53$
$\beta_1 = .059 \pm .10$
$\beta_2 = 2.63 \pm .42$
$K = -.05$

great reduction in working strength for a 12-inch diameter column due to increase in maximum size of aggregate; the maximum size must be limited to ensure a reasonable strength return. There is very little advantage in using a small aggregate in a large column, and a relatively large-size aggregate may be used with small loss in safe stress magnitude.

Since the values given in Table VIII are but tentative, if

used at all they are not to be directly applied in design, but as an aid in the selection of aggregates for preliminary tests to determine the aggregate to use in the finished product.

The safe working stress values of Table VIII suggest radical changes possible in design, due to the very large stresses to be safely used when the size of aggregate is small compared to the structural element size. One of the valuable applications should be in the slab design, where the great width would appear to predict a very high working stress. These stresses are not to be increased, however, until the theory for beams and slabs has been developed and fully substantiated experimentally.

Reliability of Concrete.—The factor $(1-\gamma\varphi(v))$ of equation 17 measures the compressive strength reliability of the concrete. $\varphi(v)$ may be used as the reciprocal indication of the reliability. The test results given in the paper show that with proper selection of aggregate size for the structural element, the intrinsic compressive strength reliability of the concrete is high. By intrinsic reliability is meant the inherent reliability of the concrete as correctly fabricated, unaffected by variation in fabricating conditions, water content, insufficient mixing, etc. The intrinsic compressive reliability of concrete made with commercial aggregate compares favorably with the strength reliability of structural steel columns.

Advantage must surely be taken of the potential high compressive strength reliability of concrete, but this will require rigid supervision and inspection during the fabrication of the concrete.

CONCLUSION.

The objective and results attained have already been given in the body of the paper. It appears advisable to summarize several points of interest here.

The strength dispersion has been previously shown to be an essential factor in safe stress determination, which is in itself sufficient reason for extensive study of that dispersion.

In the analysis of the paper, it has been shown that the strength frequency curve is of the normal form or very close to the normal form, sufficiently close to permit the normal form to be used in engineering calculations.

The magnitude of the strength dispersion has been found to

be a function of the cross-sectional area of the compression specimen, viz., the coefficient of variation varies inversely as the square root of the area of the compression specimen. To simplify treatment the coefficient of variation of a specimen of area a has been expressed as a function of the cv of a specimen of unit area, thus:

$$Cv = \frac{cv}{\sqrt{a}}.$$

The strength dispersion is a function of the age and also of the maximum size of aggregate in the mix. Reference may be made to the body of the paper.

The intrinsic compression strength reliability of concrete is shown to be high, the reliability of the structural element increasing with its size. Radical changes in design are indicated, with great saving in weight of concrete, due to this, especially in very large masses, such as dams.

It is to be hoped that basic data upon the effect of grading, maximum size aggregate in mix, age, etc., upon the dispersion will be forthcoming.

The problem of the strength dispersion of plain and reinforced concrete beams is at present under consideration.

The Electric Arc in High Vacuum. S. RATNER. (*Nature*, Oct. 15, 1927.)—The author, who writes from Columbia University, has discovered a way of getting and maintaining an electric arc in a vacuum as high as .001 mm. Under a bell-jar of 12 litres' capacity are three electrodes. Electrode *A* is a heavy block of metal which is surrounded by Electrode *B* of metal gauze or perforated plate. "Electrode *C* is composed of a circular plate and an insulated platinum strip stretched across an opening in the plate; it may be used either as a cold electrode or as a Wehnelt cathode." *A* and *B* are connected to a 230-volt line while *C* is joined to a high-potential source. Let a vacuum be produced and a discharge made to pass between *B* and *C*. Then an arc forms between *A* and *B* and continues after the high-potential discharge stops. The higher the vacuum, the less the number of volts between *A* and *B* necessary to start the arc. "At 0.001 mm. pressure, a p.d. of 60 volts across *A* and *B* is sufficient to start the arc, at 0.05 mm. 120 volts is necessary, while at 1 mm. pressure a p.d. of 230 volts is not sufficient." No data of the strength of the current are given but "many amperes" "unlimited currents" are mentioned.

With *C* as anode the arc strikes without regard to the polarity of *A* and *B*, but, if *C* is cathode, the arc forms only when *A* is anode. This property is being tested for use in rectifying currents.

G. F. S.

Frost Terms Defined. (U. S. Department of Agriculture, Clip Sheet, No. 488, November 6, 1927.)—Frosts are of agricultural significance only when they occur at the time of year when vegetation is active. During the winter months they are of little significance, except in limited areas in the South and Southwest; during the summer, except in some more elevated and northern areas, they do not occur. The last frost in the spring and the first in the fall are especially noted by observers of the Weather Bureau of the U. S. Department of Agriculture. Three distinctive frost types, based on degrees of severity, are recognized, namely, "light," "heavy," and "killing." A frost that has no destructive effect, although tender plants and vines in exposed places may be injured, is recorded as "light." The term "heavy frost" describes a condition that is in itself more severe than a light frost—the deposit of frost is heavier and the temperature falls to a lower point, although the staple products of a locality are not seriously injured. The term "killing frost" is used to define a frost or temperature condition of sufficient severity to be generally destructive to the staple products of the locality. The distinction between "heavy" and "killing" frost, therefore, refers more to the effect of the frost than to the amount of deposit. A low-temperature condition, with destruction to vegetation, may occur without an actual deposit of frost, because of cloudiness or some other cause. Such an occurrence is considered equivalent to a "killing frost" because of its effect on vegetation, and is usually called a "black frost."

SOME CRITICISMS ON ELECTRIC RESISTANCE AND ITS DERIVATIVE.

BY

H. NAKAMOURA.

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SYNOPSIS.

THERE are confusions between electric resistance and differential electric resistance. In one case resistance means original electric resistance and in another case it means differential resistance.

In this paper distinctions between them and measurements for them are discussed; thus it is made clear that alternating current bridge and also Mance's method measure differential resistance.

In any electrical network, potential difference between any two points differs in its phase with the current through it. The instantaneous value v_w of the component, which is in phase with current, of potential difference of any two points divided by the instantaneous intensity i of the current through there is defined as electric resistance of that location at that current intensity.[1] Electric resistance may be constant or may vary with current even though the location is fixed. The partial derivative of the instantaneous value v_w of the component, which is in phase with current, of the potential difference of any two points with respect to the instantaneous intensity i of current through there, or $\frac{\partial v_w}{\partial i}\Big]_i$, is defined as differential resistance [2] of that location at that current intensity.[1] This may also be constant or variable.

Differential resistance is something new and absolutely differs from alternating current resistance.[3]

Fig. 1 shows one typical curve. Resistance at P is the slope of the line which joins the point P and the origin O, or merely $\frac{v_w}{i}\Big]_{i=OM}$. Differential resistance at P is, however, the slope of the tangent of that curve at P, or $\frac{\partial v_w}{\partial i}\Big]_{i=OM}$.

[1] When there exists hysteresis or "trainage," history must be specified.

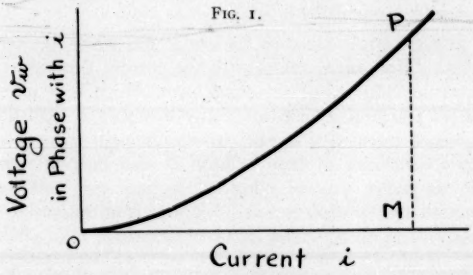
[2] This is recently called "variational resistance" by E. L. Chaffee, *Proc. I. R. E.*, **15**, p. 185, 1927.

[3] Alternating current resistance, or effective resistance, causes surrounding heat loss, radiation loss and ohmic loss, the latter of which is due to current distribution and electron configuration in the conductor.

The potential difference between any two points is generally a higher order function of the current i passing through there, so that ordinary resistance never coincides with differential resistance except when the $v_w - i$ curve is rectilinear and passing through the origin; in this case ordinary resistance is numerically equal to differential resistance.[4] As explained, resistance or differential resistance varies with current; we sometimes take average resistance or average differential resistance of any complete cycle when the current is periodic, such as alternating current.

Electric resistance has no sign; it is merely a scalar quan-

FIG. 1.



tity. In the second or fourth quadrant it may seem as if it is negative. In such case, we can draw it easily into the first quadrant by merely changing the sense of one metre. Thus, an electric arc has varying resistance[5] and varying negative differential resistance.

The word "internal resistance of a cell" may mean ordinary resistance,[6] but "internal resistance of a tiode" means differential resistance.[7]

Evidently the ordinary Wheatstone bridge[8] measures ordi-

[4] The three arms of the following bridges are assumed as such.

[5] Neither negative nor positive, or senseless.

[6] "Standard Handbook for Elec. Eng.," 4th ed., McGraw-Hill Book Co.; 8, Section 20. Sir R. Glazebrook, "A Dictionary of Applied Physics," 2, p. 62.

[7] Report of the Committee on Standardization for 1926. Ed. by I. R. E., Section 4025; J. Zenneck u. H. Rukop, "Lehrbuch der Drahtlosen Telegraphie," 5te. Aufl., S. 549.

[8] All bridges discussed here are assumed that all contact phenomena have been eliminated.

nary resistance but alternating current bridge measures differential resistance. For example, Fig. 2 shows Kohlrausch bridge for measuring the internal resistance of a cell. When no

FIG. 2.

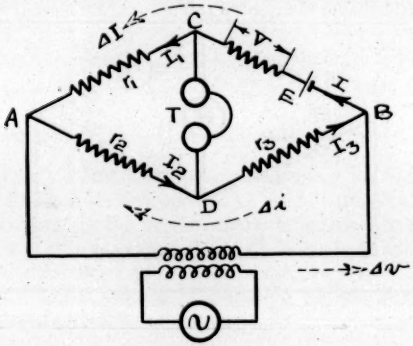
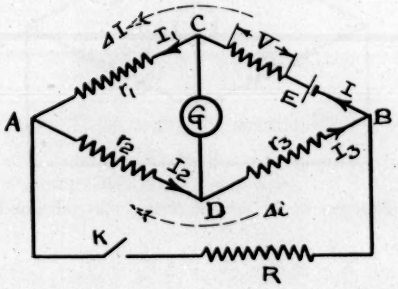


FIG. 3.



tone is heard by the telephone receiver T, the potential difference V_T between C and D must always be constant: At the instant when the oscillator generates no voltage, the following relations may be held.

$$V_T = E - V - I_3 \gamma_3$$

$$V_T = I_1 \gamma_1 + I_2 \gamma_2 ,$$

where E is the electromotive force of the cell and V is the voltage drop due to its internal resistance.

When the oscillator generates Δv, the currents in the upper and lower branches change by ΔI and Δi as indicated by dotted

FIG. 4.

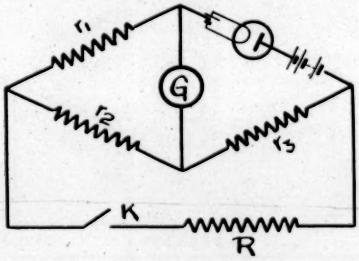
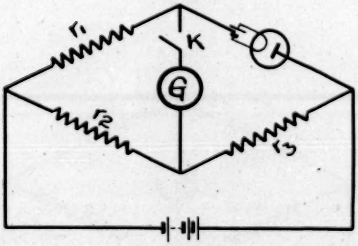


FIG. 5.



arrows. V changes by ΔV and E changes by ΔE due to ΔI.

Thus

$$V_T = E - \Delta E - (V + \Delta V) - (I_3 - \Delta i)\,\gamma_3$$

$$V_T = (I_1 + \Delta I)\,\gamma_1 + (I_2 - \Delta i)\,\gamma_2$$

$$\gamma_3\,\Delta i = \Delta E + \Delta V$$

$$\gamma_2\,\Delta i = \gamma_1\,\Delta I$$

or

$$\frac{\Delta E}{\Delta I} + \frac{\Delta V}{\Delta I} = \frac{\gamma_3}{\gamma_2}\gamma_1 .$$

That is, when the tone heard by the telephone receiver is a minimum, the following relation holds,

$$\frac{\Delta E}{\Delta I} + \frac{\Delta V}{\Delta I}\Big]_{I-\Delta I}^{I+\Delta I} = \frac{\gamma_3}{\gamma_2}\gamma_1,$$

or

$$\frac{\gamma_3}{\gamma_2}\gamma_1 \rightarrow \frac{\partial V}{\partial I}\Big]_I \quad \text{when } \Delta I \rightarrow 0,$$

if we can assume that $\frac{\Delta E}{\Delta I}$ is negligible.

Fig. 3 is Mance's method for measuring the internal resistance of a cell, in which method γ_1 is adjusted so as to give minimum change in the galvanometer deflection when the key K is opened and closed. When the key is closed the currents in the upper and lower branches change respectively by ΔI and Δi as indicated by dotted arrows. Calculating the same as above, the following relation holds:

$$\frac{\Delta E}{\Delta I} + \frac{\Delta V}{\Delta I}\Big]_{I}^{I+\Delta I} = \frac{\gamma_3}{\gamma_2}\gamma_1,$$

or

$$\frac{\gamma_3}{\gamma_2}\gamma_1 \rightarrow \frac{\partial V}{\partial I}\Big]_I \quad \text{when } \Delta I \rightarrow 0,$$

assuming that $\frac{\Delta E}{\Delta I}$ is negligibly small.

Thus both methods are suitable for measuring the differential resistance and not for ordinary resistance.

For measuring the internal resistance of a diode, Fig. 4 measures $\frac{\partial V}{\partial I}$, or differential resistance, and Fig. 5 measures $\frac{V}{I}$, or ordinary resistance where the minimum change in the galvanometer deflection is observed when the key K is closed and opened. Figs. 6 and 7 are the modifications of the alternating current bridge and measure also differential resistance. Fig. 7 is one of the most desirable methods for direct measurement of the internal resistance of a tiode.

From the above description, the author concludes that:

(1) Ordinary resistance is a mere quotient of the instan-

taneous value of the component, which is in phase with current, of the potential difference of any two points to the instantaneous value of the current passing through there and has no vectorial sense. Differential resistance, however, is the first partial deriva-

FIG. 6.

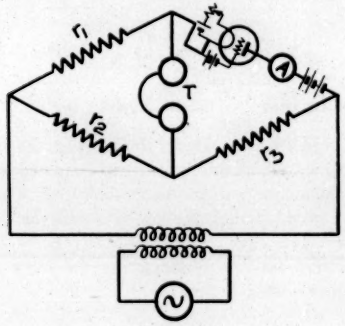
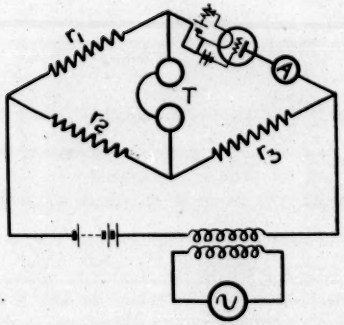


FIG. 7.



tive of the former with respect to the latter and has sense and magnitude.

(2) Wheatstone bridge and its varieties, unless balancing the galvanometer or telephone circuit by constant equipotential, measure the differential resistance and not the ordinary one.

(3) Alternating current bridge generally measures differential effective resistance. When the current is small or its effective resistance is non-directional, differential effective resistance numerically approaches to ordinary effective resistance.

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JAPAN.

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Geodetic Level Rods, Their Construction, and Method of Graduating. D. L. PARKHURST. (*J. Scient. Instruments,* June, 1927.)—"In geodetic surveying, where absolute differences in elevation must be determined with the utmost practicable accuracy, the ordinary levelling apparatus is replaced by a more accurate and sensitive instrument and a rod of special design." Before 1916 the U. S. Coast and Geodetic Survey used a wooden rod with graduations painted on its face. The wood was boiled in paraffin. This increased the weight and lowered the resiliency. In addition it was found that, while in the spring and fall, before and after the season in the field, the length of such a rod showed itself to agree with a standard, there was, however, a departure from correctness during the season. Thus errors found their way into the results.

The improved rod consists of a metal strip rigidly attached to a footpiece of steel and supported by a wooden back. The metal strip, about 3.3 metres long, is of invar with a temperature coefficient of not more than .000002 per degree centigrade. "A temperature change of 50° F., which might readily occur during a working day, will cause a difference of only about 8/1000 of an inch in the entire length, an amount which under ordinary conditions would be negligible. For the most precise work, however, this is corrected for by computation, thermometer readings of the temperature of the strip being taken while the rod is in use." G. F. S.

International Conference on Bituminous Coal.—Official announcement comes from the Carnegie Institute of Technology that a second conference will be held at Pittsburgh during the week of November 19, 1928.

Decision to call a second congress of world scientists and fuel technologists has been made, it is announced, as a result of the widespread interest aroused throughout the world by the first Conference on Bituminous Coal held at the Carnegie Institute of Technology in November, 1926.

The first conference, which was devoted to discussions of the better utilization of bituminous coal, was attended by 1700 persons, including delegates from thirteen different countries.

Although no definite program plans for the second conference have been made, it is expected that the 1928 session will cover the latest developments in obtaining substitutes for gasoline from coal, power from coal, low- and high-temperature distillation processes, smokeless fuel, gasification of coal, utilization of coal-tar products, coal as a source for fertilizer, and coal in relation to the production of fixed nitrogen.

A PROBLEM IN UNDERWATER ACOUSTICS.

BY

J. H. POWELL, D.Sc., F.Inst.P.

IN A recent communication under the above title [1] Prof. A. S. Eve has given an account of a problem which arose in the production of directional hydrophones during the war.

As the writer had the privilege of serving as a member of Professor Eve's staff engaged on the problem, the following remarks may not be inappropriate:

Attention is drawn to a paper by Wood and Young [2] dealing with this problem, in which the disturbances produced by small bodies in plane waves in water are discussed and a satisfactory approximate theory of the single plate direction finder is formulated.

Briefly, the directional hydrophone depends for its action on phase difference. In the symmetrical "edge-on" position of the unbaffled instrument, the sound waves reach the opposite faces of the hydrophone in the same phase and the diaphragm is therefore not excited.

If, however, the hydrophone is "broadside-on," the waves at the opposite faces are not in phase, a lag occurring at the back face due to the longer path travelled by the waves reaching it, and the diaphragm is excited.

The function of the baffle is to introduce a constant phase lag near the adjacent face of the diaphragm equal to the lag normally occurring at the back face in the "broadside-on" position of the unbaffled instrument. Thus when the baffled side is facing the source of sound the lags at the two faces are equal, the pulses are once more in phase, and the diaphragm is not excited. In the opposite position the two lags add, and a reinforced maximum is produced.

This elementary theory is admittedly an approximate attempt to account for a complex phenomenon, and though no simple theory covers all of the facts, some further light may be thrown on the problem from practical experience.

[1] JOUR. FRANK. INST., **202**, 627, 1926.

[2] *Proc. Roy. Soc.*, A **100**, 1921.

CHARACTERISTICS OF THE IDEAL BAFFLE PLATE.

The essential characteristic of an effective baffle is undoubtedly the air film, which is well known to act as an effective screen to sound waves in water. An air film alone, however, would be unlikely to produce good bias because of the reflection at the air-water surface which sets up secondary waves in the opposite phase. In practice the air films must be contained between solid walls and the problem becomes still more complex, since these bounding walls, unless very thick and massive, will themselves vibrate and so become secondary sources.

In the ideal baffle a compromise is reached by enclosing the air film between a thick wall on the side away from the hydrophone, and a thin diaphragm on the side facing the hydrophone. This diaphragm is aperiodically damped.

It is clear that the damping of this diaphragm must be accurately adjusted, for if it is too large reflection will take place, while if too small the diaphragm will vibrate and become a secondary source. In other words, the baffle must be such that all the energy falling upon it is dissipated in the damping medium, and neither reflected nor used in setting up vibrations in the diaphragm.

In the lead-wood baffle, the lead itself provided this damped diaphragm, the wood core being merely a non-resonant backing to produce stiffness.[3] In the xylonite-shot baffle the diaphragm was damped by the lead shot touching it at a definite number of points uniformly distributed over its surface.

In the hand-made experimental lead-wood baffles, it was possible to adjust the degree of damping in the lead sheet during construction, but when produced by machinery in quantity, no such adjustment was possible, for the lead sheet was rolled smooth, and tightly soldered over the wood core. It was sometimes possible to produce fairly good results with such baffles by simply hammering the lead surface, but such treatment naturally did not give consistent results.

The secret of the success of the xylonite baffles lay in the fact that with the same stock of xylonite, conditions could be repeated

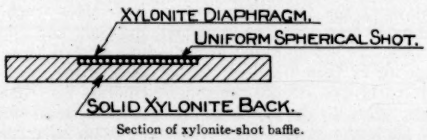
[3] The presence of air in the pores of the wood was found to modify the action of these baffles; in later baffles of this type the core was always boiled in oil to exclude the air.

exactly in any number of baffles. The shot were arranged in a single layer (Fig. 1) and were given just enough freedom to move, a definite number of spherical shot were placed in each baffle, and these could only take up one definite configuration. The series of loose contacts over the surface of the xylonite diaphragm produced a definite degree of damping which could be reproduced.

With the irregular shot the conditions ceased to be reproducible, for the shot were irregular in shape as well as in size, some being definitely ellipsoidal, and therefore neither the number of points of contact nor their positions were calculable. Such baffles failed to produce bias, and merely reduced the hydrophone to a non-directional instrument.

The distance at which a baffle is most effective depends mainly

FIG. 1.



Section of xylonite-shot baffle.

on its effective area, and in the case of the lead-wood baffles this was never constant. With the xylonite baffles the distance was always about four or five inches from the diaphragm, but each instrument required individual adjustment.

A good baffled instrument gave equally definite indications with ship sounds and general noises of all kinds, but with a source of sound giving a pure tone there was generally a best frequency for good indications, and the best position of the baffle was found to vary with frequency. This may be attributed to the fact that a normal ship noise does not possess any definite pitch, but consists, as far as at present known, of a train of low-frequency impulses which excite the diaphragm of the hydrophone and cause it to vibrate with its own natural frequency. The setting of the baffle for a ship noise is therefore that for a sound of the same frequency as the diaphragm.

In conclusion it may be stated that an approximate working solution has been obtained, but a great deal of detailed research will be necessary before the problem can be regarded as being completely solved.

Margarine.—According to J. S. ABBOTT (*Inst. Margarine Manufacturers, Bull. No. 10*, 1–23, 1927), two kinds of margarine (oleomargarine) are manufactured in the United States; the one variety is made from both animal and vegetable fats, milk and salt; the other variety is commonly called nut margarine and is made from vegetable fats, milk and salt. The fats used are oleo oil, oleo stock, oleo stearin, neutral lard, peanut oil, cottonseed oil, coconut oil, and butter. Oleo stock is beef fat rendered at a low temperature. When oleo stock is permitted to stand at a low temperature, the oleo stearin crystallizes and separates, while the oleo oil remains a liquid. Some stearin remains in the oil, and some oil in the stearin, while the palmatin is about equally divided between the oil and the stearin. The fats used vary with the brand of margarine.

In the process of manufacture, milk is pasteurized, inoculated with a starter, and ripened. The ripened milk and the fats and oils are mixed in the proper proportions, and complete emulsification is produced in a churn or other suitable apparatus. The resulting emulsion is drawn off gradually into a spray of ice water to produce crystallization of the fats. The product resembles freshly churned butter. The excess water is removed and salt and, occasionally, artificial color, are incorporated in a machine known as a "worker." The margarine is then moulded or cut into prints, and packed in cartons by machinery. Since the constituent fats vary in color from almost pure white to deep yellow, margarine without any artificial color may show the same range of color. Artificially colored margarine is subjected to a federal tax of 10 cents per pound; and only about 4 per cent. of the total output of the United States in 1926 was artificially colored. Margarine has an energy value of approximately 3500 calories per pound, and is 97 per cent. digestible.

During the fiscal year ending June 30, 1926, the following amounts of foodstuffs were used in the United States in the manufacture of margarine: Coconut oil 98,307,340 pounds, cottonseed oil 25,608,311 pounds, neutral lard 25,172,425 pounds, oleo oil 47,418,248 pounds, oleo stearin 5,313,502 pounds, oleo stock 3,082,251 pounds, peanut oil 5,257,202 pounds, salt 20,592,622 pounds, milk 72,662,310 pounds, butter, 2,330,320 pounds. The United States also exports large quantities of raw materials for the manufacture of margarine abroad; in 1925, in round numbers, these exports included 92,000,000 pounds of oleo oil, 19,000,000 pounds of neutral lard, and much larger quantities of cottonseed oil. At the present time, 61 margarine factories are in operation in the United States. The annual business of the industry amounts to almost $100,000,000. J. S. H.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

SEVENTH INTERNATIONAL CONFERENCE ON WEIGHTS AND MEASURES.

A REMARKABLE advance toward complete international agreement on fundamental questions of measurement took place at the Seventh International Conference on Weights and Measures, held last September in Paris. At this conference the United States was represented by the Director of the Bureau of Standards. The present year is the fiftieth anniversary of the establishment of the International Bureau of Weights and Measures and in commemoration of the event a special meeting was held under the auspices of the French Academy of Sciences in connection with the conference. A history of the International Bureau by its director, Dr. Ch.-Éd. Guillaume, was published and gives an interesting review of past achievements.

The conference just held was the most important in point of results secured since the first conference in 1875. The actions taken affect fundamentally many kinds of measurements and standards and are based on the results of painstaking scientific research, covering many years. The new decisions involve the international temperature scale, the fundamental standard of length of the world, and the basis of the world's electrical units.

Under the treaty of May 20, 1875, there was established the International Committee on Weights and Measures, the International Bureau of Weights and Measures, and the International Conference on Weights and Measures. The treaty, to which thirty-one of the leading governments are now parties, gives the conference jurisdiction over the fundamental problems affecting the international metric standards and precise metrology. The royal grounds and residence at Sèvres, set aside by the French Government, were made internationally neutral territory to be devoted to the International Bureau of Weights and Measures where the international standards were to be deposited and the precise comparisons of national standards executed from time to time. Here were made the final standards of the metre and kilogram and here these standards were intercompared for distribu-

* Communicated by the Director.

tion to the various governments of the world. This historic centre is now replete with records of achievements in the science and art of measurement during the past half century.

The international conference meets once in six years and is made up of delegates from the thirty-one national governments. Adoption of any proposition by the conference can only be secured by the unanimous vote of all nations represented, each nation having one vote. The recommendations of the conference are, in effect and when ratified, binding on the signatory powers, and because of this fact and because unanimous agreement is required for adoption, the process of effecting important changes is usually slow.

Immediately before the conference just held the Director of the Bureau of Standards met with the representatives of the national laboratories of Great Britain and Germany, and in an informal conference these three nations agreed on every value for the international temperature scale. These values were accepted by the international conference, with the understanding that a special international committee would be chosen to study the matter of temperature measurements and recommend such revisions as may be found necessary from time to time in the future.

The significance of the final adoption of the international temperature scale by thirty-one nations is a matter of such great interest to science and industry that a brief summary of what this involves should be given. The action assures the following desirable ends:

(1) A uniform basis for expressing all quantities involving temperature and heat measurement such as tables of properties of refrigerants, steam tables, heats of combustion, specific and latent heat of materials, and particularly fixed temperatures such as freezing, boiling, and transition temperatures of substances.

(2) A uniform basis for calibration of all temperature measuring instruments, particularly those for export from one nation to another. This is particularly important in the case of pyrometers for use at very high temperatures.

(3) A common basis in all countries for the certification of precision temperature measuring instruments for use in all precise experimental or research work involving temperature measurements. Such basis is now so well defined and universally understood as to make it unnecessary for the researcher in publishing

his results either to establish or define his own temperature scale as has often been necessary in the past.

(4) While for a number of years the three national laboratories of England, Germany, and the United States have been in substantial agreement in the certification of temperature measuring instruments, the adoption of their recommendations by the international bureau will have the effect of bringing all the important countries of the world together in the matter of temperature measurements, and will stabilize the basis of temperature measurement and eliminate differences in details. The desire to eliminate such differences has already led the laboratories to make intercomparisons of calibrated instruments in preparation for the formal adoption of the scale, and this interchange will lead to the establishment of closer and more cordial relations.

(5) It is also significant that each of the laboratories has been willing to modify its position where necessary since it was apparent to all that international agreement was of much greater importance than precise adherence to the practice of the individual laboratories.

The proposition of the United States to define the length of the international metre in terms of the wave-length of the red radiation from the cadmium lamp was also tentatively adopted, the final wording of the recommendation as decided upon by the conference being an improvement on that submitted by the United States. As a result of this action, there is now established a permanent natural standard of length, easily reproduced, and capable of being used in the most precise measurements we are ever called upon to make. Although the particular line chosen in the spectrum of cadmium is believed to be a very good one for this purpose, the way has been left open to utilize a better line, such as one of those in the spectrum of Krypton, if future investigations prove this to be desirable.

The conference tentatively adopted the value determined by Fabry and Perot in 1906 as expressing the relation between the international metre and the wave-length of red light from cadmium vapor. This relation is

$$1 \text{ metre} = 1\,553\,164.13 \text{ waves}$$

under certain definitely stated standard conditions.

The wave-length of cadmium light is thus accepted as a

standard in terms of which lengths may be measured and other light wave standards may be expressed. This action is of great importance because of the fact that many precise length measurements in science and industry are now made in terms of light waves, and is particularly useful for setting up and intercomparison of gauge blocks and other subdivisions of the metre.

It was also the hope of the United States delegates that the conference would adopt or recommend a definite relation between the yard and the wave-length of light, or between the yard and the metre. The adoption of such a relation is equally important, since it would overcome a difficulty which often arises, that is, of converting wave-lengths to inches, a different relation being used in this country and in Great Britain.

This agreement on the length of the British and American yards, which now differ by a few millionths of an inch, unfortunately was not brought about. Research is now in progress in England on the length of their national standard, and pending the completion of this work it appeared impossible to reach an understanding. The difference is very small but is becoming of importance in making some of the finer measuring tools now used by industry. It was held by the conference, however, that the relation between the yard and the metre, or between the yard and the wave-length of light, was a matter that should be settled by the United States and Great Britain rather than by the international conference, and no action was therefore taken. However, the British delegates expressed themselves as heartily in favor of the idea, and agreement between the systems of the two countries will undoubtedly be brought about in time.

The matter of standard temperatures at which end standards (gauge blocks) shall be certified was also considered in connection with length measurements. It is desirable to employ a temperature or temperatures at which the blocks are actually used. At present, there are many variations in the practice of different nations. A committee will be chosen to consider the question and if possible agree upon not more than two standard temperatures at which end standards will be certified.

The third major problem considered by the conference was the standardization of the electrical units and the scope of the international bureau in relation to electrical measurements.

Up to the present time international agreements with regard

to electrical measurements have been made by electrical congresses and international committees formed for this specific purpose. The number of international organizations has, however, multiplied so greatly that it has become desirable to combine them and reduce the number of special organizations. In accordance with this general principle the international conference has been authorized to establish electrical units.

The United States is concerned with maintenance of international uniformity in electrical measurements for two practical reasons. One is the need for uniformity in manufacture and rating of electrical machinery and appliances and the other the international use of the results of scientific research. In order to bring about such uniformity, agreement was reached many years ago on certain electrical units which were called "international" to distinguish them from the "absolute" values which might be found more or less different from the accepted units as methods of measurement were perfected. In fact, such a difference has been found in the case of the ohm, and we now know that the international ohm is one-twentieth of 1 per cent. too large. While such a difference is of no great practical importance at the present time, the demands of industry for precise measurements are growing rapidly and such a difference may become important in the future. The international committee must therefore decide whether to maintain the old value of the ohm or to adjust it to accord with mechanical measurements as originally intended.

When the international units were adopted certain kinds of concrete standards were also accepted as a means of maintaining the values of the unit. These are a column of mercury of specified dimensions for the ohm, and a voltmeter in which the amount of silver deposited in a given time by a current is used as a measure of the ampere. The international committee must decide whether to retain these old standards or to substitute new methods of establishing the units which have been developed in the several national laboratories.

In order to advise it as to the best solution for these questions, the international committee is establishing a special technical commission of ten members, including representatives appointed by the several national laboratories, and is to report by March, 1929.

For several years the Bureau of Standards has been putting as much attention as it could on these fundamental electrical problems and has already made some redeterminations of the true value of the ohm and the ampere by absolute methods. In order to be of value the results of such work must be certain to within a few parts in 100,000, and therefore many precautions must be taken which are entirely unnecessary in any ordinary measurements. The work is therefore very time-consuming and still more intensive effort must be put upon it in order to have results available by the spring of 1929.

COÖPERATIVE MEASUREMENTS OF RADIO FADING IN 1925.

AT THE beginning of 1925 the bureau invited a number of laboratories to participate in a coöperating program of radio measurements. This work, which was continued for a year, was largely confined to measurements of fading at frequencies within the broadcast band. The general plan of the work was the arrangement of special transmissions in which a station transmitted continuously during a specified period while the observing laboratories made graphic records simultaneously, employing the method previously used by G. W. Pickard.

The investigation included observations during the solar eclipse of January 24th, during many sunset periods, and during a complete twenty-four-hour cycle, in addition to a special study of the effect of high power on fading. The analysis of more than 150 graphic records made by twenty-three coöperating laboratories located in northeastern United States and Canada established a number of new facts about fading and radio wave transmission.

Among the principal conclusions resulting from the research are the following:

(1) There is a degree of regularity in the average intensity during conditions of fading which has not hitherto been suspected. The ratio of average night to day intensity has a logarithmic relation to distance.

(2) There are indications of series of maxima and minima of fluctuation with respect to distance from the transmitting station. The first maxima occurs at about 100 km.

(3) There is some evidence of correlation between direction shifts and fast fading.

(4) The maximum diurnal intensity appears at about the same time (during the three hours just preceding sunrise, in December) at all receiving points within 500 km. of the transmitting station (this conclusion is based on a single twenty-four-hour observation period).

(5) There is sometimes a special periodic type of fading, beginning about 15 to 20 minutes after sunset, of great regularity, the periodicity of which shows a correlation with the distance between the transmitting and receiving points, and which is evidently due to an interference phenomenon.

(6) Changes of transmitting power do not affect the characteristics of fading.

A more complete description of the method and results of this investigation have just been published in Scientific Paper No. 561, "Coöperative Measurements of Radio Fading in 1925," by J. H. Dellinger, C. B. Joliffe, and T. Parkinson. This paper can be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., at fifteen cents per copy.

PROGRESS REPORT ON THE MECHANISM OF COLOR SENSITIZATION AND HYPERSENSITIZATION.

THE work discussed here is part of a more comprehensive program of research on the mechanism of sensitization by dyes for new spectral regions. It is based on observation of three factors, which we may predict from well-known principles of colloid chemistry to be of importance. These are, as usual, by no means completely independent, but they may logically be taken up as distinct topics.

The sensitivity to white light (total sensitivity) was measured by the standard methods, using an incandescent light corrected by Corning glass to give a color match with Priest's artificial sunlight. The sensitivity conferred by the dye was judged from a sensitometer test in which a Wratten "Minus Blue" filter was inserted between the light source and plates, *in addition to* the correction filter. The *"Minus Blue"* filter "cuts" very sharply at approximately 500 millimicrons; the speed of these emulsions without dye is almost zero through this filter, while practically all the radiation for which any of the dyes (except pinaflavol) sensitize, is freely transmitted. For brevity, the

speed measured in this way will be called "M.B." speed. It is $10/i$, where i is measured in candle-meter-seconds of sunlight quality *incident* on the minus blue filter. An interesting feature of all the data is the higher gamma for the exposures behind the minus blue filter; the effect has been known in practical three-color work for some time, but only recently confirmed quantitatively, and the magnitude is rather striking, ranging from 15 to 50 per cent.

The dyes used in sensitizing are closely restricted in type and limited in number, but of the two types in common use, one is acid and the other basic.

The acid type is the eosins, halogen substitution products of fluorescein, and of these only one is believed to be in regular use; this is erythrosin, tetraiodofluorescein, and practically all orthochromatic emulsions are sensitized with this dye, while it is the green sensitizer of most panchromatic emulsions. It is regularly used as the sodium salt, which is soluble in water to the extent of more than two grams per litre, and may be assumed to ionize to the positive sodium and negative dye ions; the concentration of dye ion should be reduced by increasing hydrogen-ion concentration (decreasing pH), since the dye acid is very weak and very slightly soluble. According to the present theories, the negative dye ion would be adsorbed at a silver ion of the silver bromide crystal lattice.

The basic dyes are extremely complex quarternary nitrogen bases, derived from quinoline or pyridine; there are several subgroups, such as isocyanines, carbocyanines, etc. These dyes are the halogen salts of nitrogen bases; they are slightly soluble in alcohol, pyridine and some other organic solvents, but almost insoluble in water, in which they form colloidal suspensions. The trace which is in true solution in water should ionize into negative halogen, and positive dye, ions; the dye ion would be adsorbed at a bromide ion of a silver bromide crystal. Increasing hydrogen-ion concentration would not affect the ionization, but converts the dyes, at varying pH's depending on the dye, into colorless forms which naturally do not sensitize; the color and sensitizing properties return with return of the reaction to neutrality, if the acid treatment has not been too severe. Traces of soluble halide would, on the other hand, strongly repress the dissociation; since the concentration of halide ion in equilibrium

with the solution of the pure dye is almost infinitesimal, although real. These dyes are very possibly adsorbed best from colloidal suspension rather than from true solution, since the resulting sensitization from a given bath rapidly decreases as water is replaced by alcohol or pyridine in the solvent mixture. It has recently been determined that the adsorption of orthochrome T (one of the isocyanines) decreases with decreasing pH.

I. *Mutual Effect of the Dye and After-ripening.*—Ripening of the emulsion after washing must consist almost entirely in the formation of nuclei on the *surface* of the grains, since in the absence of solvents, such as ammonia or soluble bromide, the recrystallization is entirely negligible. The presence of dye adsorbed to the surface would, therefore, be expected to influence the after-ripening. We had previously observed a retardation of storage ripening (in the dried plates). The experiments were extended to include digestion of the emulsion in the washed state before coating. Experiments were made both with neutral and ammoniacal emulsions; both deteriorated seriously in five months, either from the use of a new make of gelatin or from unfavorable conditions of storage; and with the ammonia emulsions, this goes so far as to interfere with judgment of the results in some cases. The after-ripening and deterioration through fog, while not independent, are not necessarily affected in the same way by the dye.

On the basis of the results available to date, the after-ripening judged by change in white-light speed is retarded but not stopped by pinacyanol or pinaverdol; this applies either to digestion or storage ripening. The M.B. speed with pinacyanol is approximately constant, during after-ripening which may amount to 100 per cent. on white-light sensitivity. A pinaverdol-sensitized batch gave a distinct increase in M.B. speed, but the filter factor increased on storage. Erythrosin (one case) did not appear to retard the after-ripening at all, and the filter factor actually decreased during storage. It is quite possible that the erythrosin will be found fundamentally different from the basic dyes in this respect. It is also practically free from the tendency to cause fog, which is one of the serious difficulties in using the basic dyes. We found (in two cases, with pinacyanol) that a batch of emulsion first digested, then sensitized, fogged less on storage than other batches of the same emulsion which were, respectively,

digested with the dye, and sensitized without digestion. In other words, there was more fog when all the after-ripening occurred in the presence of the dye, than when most of it took place first, as would be expected; and furthermore the dye is to some extent a protection against *storage* fog.

Six emulsions, each subdivided into from four to eleven batches, still remain to be tested for keeping qualities.

II. *Effect of pH on Color Sensitivity.*—The sensitivity of any silver bromide-gelatin emulsion, with or without dye, increases with increasing pH during digestion and at coating. Superimposed on this is a change in the relative color sensitivity (filter factor), the contribution by the dye increasing faster than the total sensitivity. It is still open to question whether ammonia hypersensitization is not merely a matter of increasing pH, although a specific action of nitrogen bases such as ammonia is probable. Erythrosin becomes less ionized and less soluble in solutions of increasing hydrogen-ion concentration (decreasing pH), while pinacyanol should be less affected. If the ion, rather than the molecule, of the dye is adsorbed, erythrosin should then be the more affected by changing pH, and we actually find that this is the case. The relative color sensitivity of erythrosin-sensitized batches of a given emulsion decreases more rapidly with decreasing pH than does that of the pinacyanol-sensitized batches.

III. *Effect of Soluble Bromide on Color Sensitivity.*—The marked reduction in color sensitivity produced by traces of soluble bromide is most probably caused by selective adsorption of the bromide instead of the dye. The dyes are complex compounds of high molecular weight (300 to 700), and are used in very small amounts, so that traces of soluble bromide added as preservatives are likely to be much the larger when expressed in terms of chemical equivalents. For example, taking approximately optimum conditions, a litre of emulsion is sensitized with 5×10^{-6} mol. of pinacyanol or 2×10^{-5} mol. of erythrosin. The addition of 5 c.c. of N/100 soluble bromide, or 5×10^{-5} mol., is necessary to produce any marked improvement in the stability, and this increases the filter factor by an average of 50 per cent. in the erythrosin-sensitized emulsions. The results with pinacyanol were less consistent, but it appears to be less sensitive to bromide than the erythrosin. The effect on the erythrosin would

be predicted from the fact that both bromide and erythrosin ions are adsorbed to the silver ions of the silver bromide lattice. The effect on the basic dyes is most readily explained by the decrease in their true solubility on addition of soluble bromide; this has recently been proved by experiment.

We propose to cover the following additional points in continuing the investigation:

(*A*) Further study of the effect of pH on sensitivity, including:

(1) Comparison of hypersensitization by solutions of given pH of ammonia, pyridine and other nitrogen bases on the one hand, and nitrogen-free bases such as borax and sodium carbonate on the other.

(2) Comparison of the relation between pH and sensitivity for pinacyanol and for dyes such as kryptocyanine which are decolorized at higher values of pH.

(*B*) Effect of the ratios of soluble bromide to dye, as well as the ratio of soluble bromide to silver bromide. (The grain size, or rather specific surface of the silver bromide, will have to be considered in this connection.)

(*C*) The possible hypersensitizing action of silver bromide solvents, such as potassium cyanide, which act in such low concentrations that they do not coagulate dyes; the possibility here being that dye would be absorbed better at a freshly etched surface.

FLUORESCENCE AS A MEANS OF DETECTING THE ADMIXTURE OF REFINED IN UNREFINED EDIBLE OLIVE OIL.

Unrefined (particularly natural or virgin) olive oil is considered superior to refined olive oil, and has thus a higher commercial value. Some visitors recently brought to the bureau samples of olive oil alleged to be 100 per cent. natural, 100 per cent. refined, and various mixtures of natural and refined, as well as various other samples, some labelled as virgin, all of European origin. The difference in color between the alleged 100 per cent. natural oil and the 100 per cent. refined oil was not great, chemical tests for differentiating the two were said to be

inadequate, and it is apparently difficult even for an expert taster to be certain of his conclusions. As a result it is claimed that much of the imported olive oil labelled as virgin oil is in reality adulterated with a considerable proportion of refined oil.

However, information had been obtained that an instrument was now being used in France by means of which small admixtures of refined olive oil in unrefined oil could be detected. It was said that this instrument made use of the "365 ray." Acting on this information, the oils submitted were examined with ultra-violet energy, using a quartz-mercury lamp and Corning ultra-violet filters. The resulting fluorescence was quite striking. The alleged 100 per cent. natural oil showed a yellowish fluorescence, very similar to the color of the oil by daylight, the alleged 100 per cent. refined oil showed a bluish fluorescence and mixtures of natural and refined showed intermediate colors. All of the samples of European origin so far examined show a fluorescence which may be placed (at least approximately) somewhere in the color sequence between the alleged 100 per cent. natural and 100 per cent. refined oils.

On the other hand, a sample of California pure unrefined olive oil obtained from the Bureau of Chemistry, said to be of high chlorophyl content, showed a much redder fluorescence than the European oils; and a sample of this same oil refined in the Bureau of Chemistry laboratories showed but little indication of the bluish fluorescence. The question may therefore be raised as to the general applicability of this method of examination.

Since these experiments were made it has been learned from L. J. Buttolph, of the Cooper Hewitt Electric Company, that similar tests have recently been made by others using their mercury lamps. Beyond this, there seems to be very little knowledge of this matter in America. Inquiry of a number of leading chemists in the vegetable oil industry has failed to elicit any information concerning it. So far as we know, the observations concerning the difference between the behavior of European and California oils in this test is new. Further investigation will be necessary to decide whether or not this test may be relied upon in all cases to distinguish certainly between unrefined and refined oil; but it may be said that the test is very simple and convenient and the results have been very striking for the samples submitted.

An account of the experiments made by K. S. Gibson at the

Bureau of Standards was communicated (orally, by I. G. Priest) to the meeting of the American Oil Chemists' Society in New York, October 28, 1927.

CARBOHYDRATES TO BE STUDIED BY NATIONAL RESEARCH COUNCIL FELLOWSHIP.

Dr. W. C. Austin has recently been appointed a research associate in the sugar section of the Bureau of Standards, having been granted a fellowship by the Medical Fellowship Board of the National Research Council. His subject will be "Carbohydrates." The question of metabolism and carbohydrate structure is deemed an important subject for investigation, as but little information is available on that important relation which exists between the structure of the sugars and the human physiology and metabolism. This borderland is a most difficult field in which to carry out experimental investigation and requires investigators with a knowledge of both the subjects of metabolism and carbohydrate structure.

GUAYULE RUBBER.

The use of guayule in place of Hevea rubber would prove of great economic value to the United States, as the shrub from which it is produced can be successfully grown in southwestern United States, California and Mexico. The results of a study recently made of this rubber are presented in Bureau of Standards Technologic Paper No. 353, entitled, "Some Vulcanization Tests of Guayule Rubber." This paper gives the results of some physical tests of guayule rubber grown in both Mexico and California. The samples of guayule rubber were obtained from shrub which had been harvested and treated, the rubber being forwarded to the Bureau of Standards. Figures are given showing the properties of different types of guayule rubber and several compounds made with standard plantation crepes. Tests were made using "pure gum," zinc oxide, and gas-black formulas, and also in formulas where one-half the guayule rubber was replaced with plantation crepe. Some data are given on the aging properties of compounds based on eight months' exposure to the weather protected from sunlight. The results indicate that properly prepared guayule rubber will compare favorably with plantation Hevea rubber.

Copies of this publication may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., at five cents each.

COPPER NUMBER OF PAPER.

"A MODIFIED Method for Determination of the Copper Number of Paper" is the title of Bureau of Standards Technologic Paper No. 354, recently issued. By the term "copper number," as applied to the examination of celluloses, is meant the amount of copper reduced from Fehling solution by a given amount of cellulose material. This determination is used to find the content of oxidation products and other degraded celluloses, the strength and durability of the cellulose material being adversely affected by such constituents. It is applied to paper to find its probable resistance to chemical deterioration and to study the effect on the paper fibre of the various chemical processes used in manufacturing the paper.

A modified method was developed especially for use in determining the copper number of high-grade, glue surface-sized, rag bond papers. Such papers are very tough and hard, and owing to their resistance to disintegration and to permeation by liquids, satisfactory analytical results are difficult to obtain by the usual procedure. The method is patterned after the method of Gault and Mukerji and that of Staud and Gray. The variation from these methods considered of prime importance is grinding the test specimens to a finely divided condition, this being found essential for obtaining uniform and accurate test results. Such procedure also is an advantage in that it reduces the time required for treatment of the paper in the various analytical manipulations. A grinder devised especially for treatment of paper is described in detail.

Copies of this paper may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C., at five cents each.

STUDY OF GLASS TANK BLOCK.

A TEST, forming the ninth and last of a series on glass tank blocks, included in an investigation on glass tank block corrosion, has recently been completed. The test consisted of melting 400 pounds of glass per day for thirty days at an average tem-

perature of 1400° C. The last tank contained clay blocks furnished by two manufacturers, and so-called special refractories as andalusite, mullite, and sillimanite were furnished by four manufacturers.

The porosity and relative pore size, which were determined on cylindrical specimens approximately 2 inches in diameter and 3 inches high, are as follows:

Block.	Porosity.	Pore Size.*		
		Large after 20 Min.	Medium after 72 Hrs.	Small after Boiling.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
A	28	90	3	7
B	30	88	2	10
C	26	91	4	5
D	22	90	2	8
E	Negligible	..	..	..
F	Negligible	..	..	..
G	10	92	2	6

*The pore size was determined from the rates of absorption of water after 20 minutes, 72 hours, and boiling.

A preliminary petrographic examination of the various blocks gave the following information as to their composition:

A. (Clay block.) Largely small, poorly developed mullite, with interstitial glass.

B. Largely corundum and andalusite, with smaller amounts of mullite and quartz and a little glass.

C. Largely very minute crystals of mullite in glass, with remnants of undissociated cyanite grains at their centres.

D. (Clay block.) Largely minute crystals of mullite embedded in considerable glass, with indications that much solution of the quartz grains has taken place.

E and *F*. Mainly corundum with some glass, and with some minute needles of mullite in the latter.

G. Largely coarse grains of corundum and mullite with interstitial glass.

Blocks *E* and *F* showed the least amount of corrosion with blocks *B* and *G* not materially more affected. However, blocks *G* and *E* cracked some time after installation. Block *F* was received partially cracked and this crack continued through the entire block sometime during the test. Of the special refractories, block *C* showed the greatest amount of corrosion. The surface of this block exposed to the glass was badly pitted and

had a spongy appearance. The two clay blocks compared favorably with the best of this type previously tested in resistance to the corrosive action of the molten glass. Blocks *A*, *C*, and *D* may have shown less resistance to attack because of poorly developed mullite crystals and a larger proportion of interstitial glass in combination with a relatively high porosity. The physical structure of the blocks, prepared from special refractory material, appears also to have a direct relation to their resistance to corrosion by the molten glass.

PHYSICAL PROPERTIES OF COMMERCIAL ENGLISH CHINA CLAYS.

AT THE Columbus branch of the Bureau of Standards, work on the china clay investigation during the past few months has included the evaluation of properties at high temperatures. Specimens of the seventeen English clays being studied were fired to cones 18 and 23 (1490 and 1590° C.) and the softening points were obtained in the standard manner through a study of cone deformations. A summary of the results of this work may be of interest and is presented herein.

The specimens were the standard size bars used for such determination. A schedule of 24 to 30 hours was used in making the burn. An average of five tests was taken to obtain figures for all properties, with the exception of the modulus of rupture, where the figure was taken from ten tests. The variation from one clay to another is so slight (less than 8 per cent. on the average) that it seems justifiable for the present purposes to average all seventeen clays for each property at each firing temperature, and upon this basis the following table is obtained:

Cone.	3	5	8	11	14	18	23
Volume shrinkage (per cent.)	20.0	26.3	32.5	41.7	48.8	48.5	48.5
Porosity (per cent.)	40.29	35.92	28.96	17.49	3.85	1.22	1.01
Bulk specific gravity	1.60	1.75	1.91	2.17	2.45	2.50	2.50
Modulus of rupture	....	....	2219	2988	4181	5512	6146

As would be expected, when the temperature of firing increases, the percentage volume shrinkage increases, the per cent. porosity decreases, the bulk specific gravity increases, and the modulus of rupture increases.

The softening point determinations were made in a small surface combustion furnace at a rate of heating of 150° C. per hour above cone 20, which is the rate used by the bureau. The clays showed remarkable similarity in this property, none of them softening below cone 33 and none above cone 35. The average is about cone 34, which corresponds to a temperature of 1740° C. or 3164° F.

COMPARATIVE TESTS ON CONCRETE CYLINDERS OF DIFFERENT SIZES.

A series of 216 concrete cylinders, mixed and made in the field, half of which were 8 by 16 inch and the remainder 10 by 20 inch, were recently tested at the bureau. The object of the series was the determination of the comparative strengths developed by the two sizes of specimens using local sand and gravel under field laboratory conditions.

The cylinders were made in a small field laboratory, the concrete being mixed in a small batch mixer. Each batch was large enough to make four 8 by 16 and four 10 by 20-inch cylinders. After mixing to the desired consistency the batch was emptied into a wheelbarrow and a shovelful was placed into each of the paper cylinder moulds in succession until filled. Each cylinder was properly tamped during filling.

Three mixes were used, 1:1:2, 1:1 1/2:3, and 1:2:4. The 1:1 1/2:3 and 1:2:4 were tested at 3, 7 and 28 days. The 1:1:2 mix was tested at 3 and 28 days. For each proportion the concrete was mixed to three consistencies, giving the approximate slumps of 2, 4 1/2, and 6 1/2. Since the cylinders in each group have the same amount of cement, water, aggregate and mixing time, the strength ratio of the 10 by 20 and 8 by 16 should be unaffected by many of the variables which enter cylinder making when duplications of mixes are attempted.

The average strength of the 10 by 20-inch cylinders was 96 per cent. of the average strength of the 8 by 16-inch cylinders. The strength ratios were 92 per cent., 98 per cent. and 96 per cent., respectively, for the 1:1:2, 1:1 1/2:3, and 1:2:4.

In connection with the testing of cylinders of several sizes, it is important to note that if tested in one machine at the same platten speed, the increase in strain will be slower for the small

specimens, a phenomenon observed and noted in the test of mine stoppings [1] and by Prof. D. A. Abram.[2] The strength ratios were opposite to what might be expected because of this effect.

STUDY OF THE FACTORS GOVERNING THE STRENGTH OF CONCRETE.

THE bureau has completed a study of the variables entering into the fabrication of concrete, in which 3000 cylinders were prepared and tested. Some tentative conclusions from these tests have already been reported in the November, 1926, Technical News Bulletin under the title "Water-cement Ratio in Concrete."

The variables studied are as follows:

(1) Quality of cement. Four brands of Portland cement with different characteristics were used.

(2) Gradation of the coarse aggregate. Eighteen gradings were studied.

(3) Ratio of fine to coarse aggregate, four ratios being used.

(4) Types of aggregates: Gravel, slag, and crushed limestone.

(5) Age. The specimens were tested at six ages, namely, 1, 3, 7, and 28 days, and 3 and 12 months.

(6) Proportions of mix. 1:1 1/2:3, 1:2:4, 1:3:6 mixes were used in most part.

The specimens were removed from the moulds at 24 hours and then placed in damp storage until test. All concrete was made of such consistency as to develop a flow of 95 as measured by the flow table, using fifteen 1/8-inch drops. The following conclusions may be drawn from the results of the tests:

(1) At the ages of 1, 3, 7, and 28 days, the variations in quality of the cement produced marked differences in the strengths of the 1:2:4 concrete. At the three-month age, however, the difference in strengths was 9 per cent. in term of the strength of the lowest one and there was about 6 per cent. at the age of one year.

(2) The ratio of the strength of the concrete made from the four cements at 28 days varied from 1.96 to 2.76 of the strength at 7 days, under the conditions affecting this series of tests.

[1] *Technical News Bulletin No. 118.*

[2] *Eng. and Chem. World,* Jan. 15, 1918.

(3) The proper ratio of fine to coarse aggregate for maximum strength depended on the type of the aggregate and its grading.

(4) In most cases, when the coarse aggregate was deficient in one or two of the smaller sizes, that is those varying between No. 4 to 3/8 inch and 3/8 to 3/4 inch, a markedly better workability, together with very little change in strength, was obtained when using a mix in which the fine aggregate was 50 per cent. of the total aggregate than when the fine aggregate was less than 33 1/3 per cent. of the total aggregate.

ERRATA.

INTEGRAPH SOLUTION OF DIFFERENTIAL EQUATIONS.

BY

V. Bush and H. L. Hazen.

Massachusetts Institute of Technology.

Through an error the Figs. 3 and 4, pages 579 and 581, November, 1927, Journal, were improperly designated. Fig. 3 should be Fig. 4 and should be placed on page 581 and the figure at present indicated as 4 should be marked " Fig. 3 " and transposed to page 579.

The Effect of X-rays upon Thermoluminescence. FRANCES G. WICK. (*J. Opt. Soc. Am.*, Jan., 1927.)—Fluorite and other materials exhibit the phenomenon of thermoluminescence, that is, they emit light when heated to a moderate temperature. Miss Wick has found that this effect is modified by subjecting the source of light to a preliminary treatment with X-rays. A specimen of fluorite from Franklin County, N. J., when heated emitted strong green light. When this specimen was subjected to X-rays and then heated there appeared first a yellow luminescence lasting a short time and then the green light. The intensity of the thermoluminescent light, in all cases orange in color, emitted by calcite was increased by letting X-rays fall upon the mineral. By such treatment one piece of calcite was caused to display a green luminescence before the orange appeared. G. F. S.

Photo-electric Cell as a Colorimeter.—STANLEY P. REIMANN, of the Lankenau Hospital, Philadelphia (*Proc. Soc. Exp. Biology and Medicine*, 1926, **23**, 520–523), uses a photo-electric cell as a colorimeter. Light from a source of illumination is passed through a colorimeter cup containing the colored solution, and the transmitted light is caused to fall upon a photo-electric cell. The current generated in the cell is then measured. The standard solution and the unknown solution may be matched by changing the height of the column of liquid in the colorimeter cup until the two solutions give the same current; or the distance of the source of light from the photo-electric cell may be varied so as to obtain the same current with both solutions, keeping the height of the liquid in the cup constant. The concentration of the solute in the unknown is then calculated. J. S. H.

Oxidation of Meteoric Iron.—EARL V. SHANNON (*Proc. U. S. National Museum*, 1927, **72**, Article 21, 1–15) has investigated the oxidation of meteoric iron and reached the following conclusions. Magnetite is formed only in relatively small amounts as a transitory and unstable stage in the oxidation. The magnetite and the iron itself are rapidly converted into limonite or ferric hydroxide without the intermediate formation of ferromagnetic ferric oxide in appreciable amounts. However, meteoric iron contains nickel, cobalt, and copper. During the oxidation, persistent ferrites of these metals, *e.g.*, trevorite or nickelous ferrite $NiO.Fe_2O_3$, are formed. They are strongly ferromagnetic, and their presence accounts for the magnetic properties of the resulting mass. No evidence exists of the formation of any ferromagnetic oxide other than the ferrites of the bivalent metals. The sole function of chlorides in these changes apparently is to promote the formation of the amorphous ferric hydroxide from the metal. Terrestrial occurrences of ferromagnetic ferric oxide have a different composition and origin, and present no analogies to the oxidation of meteorites. J. S. H.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

THE TRANSPARENCY OF TURBID MEDIA.[1]

By L. Silberstein.

THE paper deals with the transmission of light through a layer of absorbing and scattering particles. It is assumed that of the light scattered, or re-scattered, by each particle a certain fraction (ζ) is sent forward and the remainder backward, the numerical value of this fraction being left free. A particle struck by directly transmitted, collimated light of intensity I is assumed to scatter (per unit time) the amount AI and to absorb κI. The same coefficients A, κ, are applied also to the fluxes of light already scattered by other particles. These assumptions lead to three simple differential equations for the directly transmitted and the two scattered light fluxes, one directed forward and the other backward, say I, S, S', respectively. These equations are readily integrated. With n written for the number of particles per unit area of the layer and with the intensity of the incident collimated light, assumed as unit, the resulting formulas are

$$I = e^{-(\alpha+A)n} \tag{1}$$

$$S + I = \frac{2\beta}{(\alpha+\beta)e^{\beta n} - (\alpha-\beta)e^{-\beta n}} \tag{2}$$

$$S' = \frac{(1-\zeta)A}{2\beta}(e^{\beta n} - e^{-\beta n})(S+I), \tag{3}$$

where

$$\alpha = (1-\zeta)A + \kappa, \qquad \beta = \sqrt{\kappa^2 + 2(1-\zeta)A\kappa}.$$

The incident intensity being taken as unit, formula (1) gives the direct or specular, and (2) the total (specular + diffuse) transparency of the layer. The scattered light flux sent backward, as given by (3), tends for indefinitely increasing n to $S'_\infty = (1-\zeta)A/(\alpha+\beta)$.

* Communicated by the Director.

[1] Communication No. 318 from the Kodak Research Laboratories and published in *J. Opt. Soc. Amer.*, 15: 125, 1927.

Test for Castor Oil.—H. B. STOCKS (*Oil and Fat Ind.*, 1927, **4**, 315–319) finds that the sodium salts or soaps of the fatty acids up to and including lauric acid do not undergo appreciable hydrolysis in aqueous solution; this is also true of the soaps derived from castor oil. On the other hand, the sodium salts or soaps of the higher fatty acids beginning with myristic acid and those of the rosin acids are approximately 50 per cent. hydrolyzed in aqueous solution.

As a result of this observation, Stocks suggests the following test for the identification of castor oil and for the detection of its adulteration. Five grams of the oil are saponified by heating with a slight excess of alcoholic potash solution under a reflux condenser. The liquid is then rendered exactly neutral to phenolphthalein by means of hydrochloric acid. The alcohol is removed by evaporation. The residue is dissolved in water, cooled and diluted to a volume of 100 c.c. Then 10 c.c. of this solution is diluted to 250 c.c. with boiled distilled water, and titrated with decinormal hydrochloric acid, first in the presence of phenolphthalein, then of methyl orange. With castor oil, from 0.5 to 0.8 c.c. of decinormal acid is required to render the solution neutral to phenolphthalein, while most fats and oils require 8 to 9 c.c. The number of c.c. of decinormal acid used in titrating to neutrality to phenolphthalein may be expressed as per cent. of the *total* number of c.c. of decinormal acid used until neutrality to methyl orange is attained. With castor oil (15 samples), this per cent. ranged between 3.1 and 7.9. With 81 samples, including 20 different species of fats and oils, other than castor oil, this per cent. ranged between 15.3 and 54.0; in this series, butter fat, coconut oil, palm nut oil, cotton-seed oil, linseed oil, and sunflower oil tended to give a low per cent.; this phenomenon was due, in the case of the first three, to the presence in them of lower fatty acids. J. S. H.

Detection of Extracted Olive Oil.—In the manufacture of extracted olive oil, the usual solvent is carbon disulphide; and traces of sulphur compounds remain in the oil. To detect these sulphur compounds and thus show the presence of extracted oil, M. F. LAURO (*Oil and Fat Ind.*, 1927, **4**, 324–325) recommends the use of silver benzoate. If 0.02 gram of this salt and 5 c.c. of the oil are heated at a temperature of 150° C., the sulphur compounds in an extracted oil react with the silver benzoate to produce a reddish-black or black-silver sulphide which renders the oil opaque. The color produced is proportionate to the amount of extracted oil present.

If ethylene chloride has been used as the solvent for extraction, an extracted oil may be detected by wetting a copper wire with the oil, then heating the wire in a non-luminous flame, and noting the green coloration imparted to the flame due to the presence of chlorine derivatives in the extracted oil. J. S. H.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY AND SOILS.*

EFFECT OF HYDROGEN-ION CONCENTRATION ON THE ABSORPTION OF PHOSPHORUS AND POTASSIUM BY WHEAT SEEDLINGS.[1]

By Jehiel Davidson.

[ABSTRACT.]

WHEAT seedlings were grown in potassium phosphate solutions of different initial hydrogen-ion concentrations.

Relatively more potassium than phosphorus was absorbed by the seedlings, irrespective of the initial hydrogen-ion concentration of the solution. In the solutions with initial hydrogen-ion concentrations of 5.0 and lower, this preferential absorption of potassium resulted in increased acidity. In solutions with initial hydrogen-ion concentrations of 6.0 and 7.0, the increase in acidity was but slight, owing to the buffer properties of the solutions.

More phosphorus was absorbed by the seedlings from the solutions with initial pH values of 5.0 and lower than from those with pH values of 6.0 and 7.0. As all potassium salts of phosphoric acid are soluble, this tends to show that the physiological availability of phosphorus depends upon the hydrogen-ion concentration of the medium.

The general character of the results was not affected by the duration of the experiments nor by the age of the seedlings. Neither was it affected by the concentration of the solution, provided the differences in initial reactions in the solutions of the lower concentrations were maintained by daily renewal.

The excess of phosphorus absorbed from the acid solutions was found in the tops of the seedlings. The tops also had a higher potassium content than those from the neutral solutions. The roots from the neutral solutions contained more phosphorus and almost twice as much potassium as those from the corresponding acid solutions.

The power of the seedlings to absorb phosphorus and potassium decreased as they advanced in age.

* Communicated by the Chief of the Bureau.

[1] Published in *Jour. Agric. Research*, 35, No. 4, August 15, 1927, pp. 335–346.

The absorption phenomena observed in these experiments, as well as the absorption of cations and anions by living cells in general, are explained by the assumption that there is a relatively wide range in the isoelectric points of individual protoplasmic ampholytes.

STUDIES ON GLUTELINS.
II. THE GLUTELIN OF RICE (ORYZA SATIVA).[2]

By D. Breese Jones and Frank A. Csonka.

[ABSTRACT.]

THE method previously used, whereby it was shown that wheat endosperm contains two different glutelins, has been now applied to the proteins of polished rice. The glutelin was precipitated from a 0.2 per cent. sodium hydroxide extract by making the latter 0.03 saturated with ammonium sulphate. In contrast with wheat endosperm, polished rice contains only one glutelin. Percentages are given showing the elementary composition and the distribution of nitrogen in the rice glutelin. Its isoelectric point was found to be at pH 6.45.

CLARIFICATION OF STARCH CONVERSION LIQUORS IN MANUFACTURE OF CORN SUGAR AND CORN SYRUP.[3]

By M. S. Badollet and H. S. Paine.

[ABSTRACT.]

THE method of clarifying acid starch conversion liquor by the use of bentonite and sodium carbonate suggested in this paper prepares the liquor better for treatment with bone char or other activated carbon than is accomplished by the customary treatment with sodium carbonate alone, thus tending to reduce the rate of exhaustion of the carbon. If it be assumed that the colloidal material eliminated by bentonite and not by sodium carbonate would in any event be removed by the subsequent carbon treatment, then the possible commercial advantage in using bentonite clarification could be determined by comparing its cost with the saving effected by the increase in the period of use of the carbon before revivification is required.

[2] Published in *Jour. Biol. Chem.*, **74**, No. 3, September, 1927, pp. 427–431.

[3] Published in *Ind. and Eng. Chem.*, **19**, No. 11, November, 1927, pp. 1245–1246.

Sodium aluminate, which produces an effect similar to that of bentonite, is already in use with satisfactory results in the manufacture of corn sugar and corn syrup.

THE GLOBULINS OF RICE, ORYZA SATIVA.[4]

By D. Breese Jones and Charles E. F. Gersdorff.

[ABSTRACT.]

Two globulins have been isolated from the endosperm of rice, *Oryza sativa*. These proteins differ both in the temperatures at which they coagulate (74 and 90° C.), and also in their elementary composition and distribution of nitrogen. The presence of albumin could not be detected.

The globulin, albumin, and alcohol-soluble fractions obtained from commercial rice bran were also studied.

THE EVALUATION OF ETHYL EOSIN.[5]

By W. C. Holmes and J. T. Scanlan.

[ABSTRACT.]

SUITABLE gravimetric methods for the determination of eosin and ethyl eosin in samples of the latter dye are described. The methods are based upon the extreme difference in the solubility in water of the two dyes, and upon the insolubility of their color acids.

[4] Published in *Jour. Biol. Chem.*, **74**, No. 3, September, 1927, pp. 415–426.
[5] Published in *Stain Technology*, **2**, No. 4, October, 1927. pp. 101–103.

Proposed Test for Cod-liver Oil.—WALLACE H. DICKHART (*Oil and Fat Ind.*, 1927, **4**, 326–328) has studied the behavior of fish oils with uranium acetate and pyrogallic acid. Thus 10 milligrams of powdered uranyl acetate were dissolved in 5 c.c. of oil in a test-tube by heating in a steam bath for two minutes; then 5 c.c. of a 1 per cent. solution of pyrogallol in 95 per cent. alcohol were added; and the mixtures heated in the bath until most of the alcohol had evaporated. The test-tube was then removed from the bath and permitted to cool. Characteristic colors were obtained with fish oils: Cod-liver oil U. S. P. orange-red, hardened fish oil orange-red, sperm oil orange-red, sardine oil yellowish-brown, whale oil yellowish-brown, menhaden oil yellow, pilchard oil yellow, Newfoundland cod oil orange-red, herring oil light orange-red; a blank test yielded a red color. When 10 drops of a 1:4 mixture of alcohol and sulphuric acid were added to the contents of the test-tube, the color of the contents was changed: Cod-liver oil, hardened fish oil, sperm oil, and the blank were decolorized; sardine oil, whale oil, and herring oil became yellow; pilchard oil remained yellow; menhaden oil changed to a canary yellow, and Newfoundland cod oil to a bright orange.

As a result of his researches, Dickhart proposes the following test for cod-liver oil: The oil (5 c.c.) is placed in a test-tube with 10 milligrams of powdered uranyl acetate, and is then heated in the steam bath for twenty minutes, with occasional shaking. The tube is then removed from the bath; and the color of its contents is noted. Cod-liver oil U. S. P. gives an amber color which has a greenish cast in transmitted light. Norwegian sperm oil yields a light amber color, which is unaltered in transmitted light. Other fish oils yield colors as follows: Menhaden oil crimson-red, pilchard oil light red, whale oil light brownish-red, herring oil blood red, sardine oil blood red, Newfoundland cod oil blood red. This test may be used to differentiate between cod-liver oil U. S. P. and contaminated cod-liver oil. J. S. H.

Paint Retards Weathering. (U. S. Department of Agriculture, Clip Sheet, No. 488, November 6, 1927.)—Painting is the best means known for protecting exposed wood from the deterioration known as weathering, says the forest products laboratory of the Forest Service, U. S. Department of Agriculture.

Weathering is caused by the shrinkage of the surface layers of wood fibres with rapid moisture changes. Two soft-wood boards, one unpainted and one painted with three coats of ordinary house paint, were exposed to the weather for one year at the forest products laboratory. At the end of the year the edge grain of the unpainted board was already considerably "washboarded" because of the permanent "set" resulting from differences in the swelling and shrinkage of spring wood and summer wood. The only irregularities on the surface of the painted board at the end of the year were the marks of the brush.

NOTES FROM THE U. S. BUREAU OF MINES.*

COMPARISON OF OILS DERIVED FROM COAL AND FROM OIL SHALE.

By Joseph W. Horne and Arthur D. Bauer.

AN INVESTIGATION was conducted by the U. S. Bureau of Mines in coöperation with the State of Colorado, on the yields and properties of oils produced from oil shale, lignite and sub-bituminous coal, using the standard assay method developed by the bureau for oil-shale testing. The purpose of this work, which is part of the general study of oil shales being conducted by the Bureau of Mines and coöperating agencies, was to obtain information on the amount and character of the yield of crude oil or tar from different typical oil shales, the yield of light oil or naphtha that might be suitable for use in motor fuels, and other products of shale oil. As the West has large resources both of oil shale and low-grade non-coking coals, it is of interest to know the relative yields of tars, light oils, and combustible gases that can be produced from these coals when retorted under conditions similar to those suited for oil-shale retorting.

The average crude oil or tar yield of the fourteen lignites analyzed is 5.0 gallons per ton, and of the sixteen sub-bituminous coals, 12.9 gallons. The average scrubber naphtha yield of all of the samples is 1.4 gallons per ton.

The crude oils or tars produced from the coals in the assay retort had an average specific gravity of 1.009, and were difficult to separate from the water produced with them. In comparison with shale oils and petroleum, these coal tars are heavy, but in comparison with the tars, produced by high-temperature carbonization of coals, the tars are light.

The crude oils from the shales had an average specific gravity of 0.907 and could be separated fairly easily from the water produced with them. The coal tars when distilled to 275° C. produced about 45 per cent. of light oils, part of which could be used as motor fuel. These light oils contained a high percentage of compounds (average 65 per cent.) absorbed by sulphuric acid.

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About 60 per cent. of these compounds absorbed by sulphuric acid (40 per cent. of the light oils) were tar acids. This high percentage is due probably to the conditions under which the coals were retorted. The distillates from the shale oils contained about 40 per cent. of constituents soluble in sulphuric acid. These distillates to 275° C. averaged 17.3 gallons per ton of shale.

The residue of the coal tar remaining in the still after distilling off the light oils was a pitch, too thick and heavy to use as a fuel oil.

The residue of the coal remaining in the retort after carbonization was not a coke but could be classified as a char.

The coal samples used in this investigation were collected by mining engineers of the former mineral leasing division of the Bureau of Mines. The oil-shale samples were taken by engineers and chemists of the oil-shale section of the Bureau. The samples were retorted in the bureau's Oil-shale Laboratory at Boulder, Colo. The proximate and ultimate analyses of the coals were made in the coal laboratory of the Pittsburgh Station of the bureau.

A more complete report on this work has been issued as Serial 2832 of the bureau.

REDUCTION OF BREATHING LOSSES FROM VAPOR-TIGHT OIL TANKS.

By Ludwig Schmidt.

THE USE of vapor-tight tanks has proved so effective in reducing the evaporation losses of petroleum that to-day practically all operators are using this type of equipment. It has been shown, however, that vapor-tight tanks should be supplemented with additional measures which will further reduce evaporation. Probably the most effective use of the supplemental measures are found on the small producing leases where the breathing losses from vapor-tight stock tanks materially affect the volume and gravity of the stored oil. The breathing loss from a vapor-tight stock tank that is filled and emptied daily is a negligible quantity. Also, the filling loss, which on the average varies between 0.1 and 0.2 per cent., usually is not of a sufficient quantity to affect materially the value of the crude. However, the combined breathing and filling losses from a vapor-tight tank requiring several days to fill are of sufficient importance to warrant the use

of measures in addition to the vapor-tight tanks. The breathing losses are caused by atmospheric variations. Probably the greatest are the changes in atmospheric temperature which cause changes in temperature of the vapors in the tank. During the day, as the temperature increases, the gasoline-saturated vapors in the tank expand and are forced out into the atmosphere. At night the vapors are cooled and contract, drawing into the tank fresh air, which becomes saturated with gasoline vapor and is forced out of the tank during the following day. In addition to the maximum and minimum temperature variations there are many smaller variations throughout a twenty-four-hour period caused by showers, clouds, winds, and other atmospheric conditions which likewise cause the tank to breathe.

The two most common measures used by lease operators for reducing breathing losses in vapor-tight tanks are, first, operating lease tanks under pressure, and second, the use of light-colored paints and tank houses. Experimental observations have been conducted by the U. S. Bureau of Mines, in coöperation with the State of Oklahoma and oil producers, which show the reduction of evaporation losses where these supplemental measures have been used.

These tests indicate that it is doubtful if pressure alone or the use of light-colored paints, or insulation alone will be the most economic methods of reducing the breathing losses from vapor-tight tanks. It is probable that the most effective method will consist of a combination of light-colored paints and the holding of suitable pressures on the tanks. The amount of pressure required depends upon the lease operation and the physical characteristics of the oil handled. Further tests are given in Serial 2874, recently published by the Bureau of Mines.

Structure of the Methane Molecule.—VICTOR HENRI, of the University of Zurich (*Chem. Rev.*, 1927, **4**, 189–201), has applied the methods of molecular physics to the study of the molecule of methane. He decides that the methane molecule has a pyramidal, and not a tetrahedral, form, and is a labile system of atoms which is capable of change to other structures in its derivatives. He also concludes that the four valences of carbon are not equivalent, but consist of two different types. J. S. H.

Early Organic Chemistry of America.—EDGAR F. SMITH, of the University of Pennsylvania (*J. Chemical Ed.*, 1927, **4**, 1150–1157), reviews the work of American chemists in the field of organic chemistry a century ago. In 1831 Guthrie discovered chloroform; in 1832 he announced its therapeutic action as a diffusible stimulant. In 1839 Robert Hare prepared artificial camphor. His son, Clark Hare, and Boyé synthesized ethyl perchlorate in 1841. In 1842 Proctor made a study of oil of wintergreen. About this time, the fulminates also received considerable attention.

J. S. H.

Sodium Carbonate Trihydrate.—J. W. BAIN, of the University of Toronto (*Jour. Am. Chem. Soc.*, 1927, **49**, 2734–2738), has proved the existence of a trihydrate of sodium carbonate with the formula $Na_2CO_3.3H_2O$. The transition point between the trihydrate and the monohydrate, $Na_2CO_3.H_2O$ is $39.8 \pm 0.1°$ C.

J. S. H.

Heat of Formation of Zinc Oxide.—GEORGE S. PARKS, CHARLES E. HABLUTZEL and LAWRENCE E. WEBSTER, of Stanford University (*Jour. Am. Chem. Soc.*, 1927, **49**, 2792–2795), have found that the heat of formation of zinc oxide from its elements is $83{,}240 \pm 200$ calories. J. S. H.

Reinsch Test.—HENRY LEFFMANN and MAX TRUMPER (*Bull. Wagner Free Inst. Science*, 1927, **2**, 89–92) recommend that a control test be made on the reagents (copper and hydrochloric acid) before testing for the deposition of metals on the copper from the suspected material. If a metallic deposit form, the dried copper strip should be heated in a closed tube, using a spirit lamp as the source of heat. The heating should not be long continued. Arsenic gives a sublimate of bright crystals whose octahedral form is readily seen on low magnification. Mercury yields a mirror of metallic globules. Antimony gives a sublimate only if heating has been unduly prolonged; the sublimate consists in part of needle-like crystals, but is chiefly an amorphous mass. Bismuth does not give a sublimate. This test, which was first published by Reinsch in 1841, may be applied in the presence of organic matter such as the secretions and excretions, but not in the presence of oxidizing agents. Arsenites react in this test far more readily than arsenates.

J. S. H.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting Held Wednesday, November 16, 1927.)

THE regular monthly meeting of the Institute was called to order by President Wm. C. L. Eglin, at eight-sixteen P.M.

The President called for the reading of the minutes of the last meeting. The Secretary stated that the minutes of the last meeting had been printed in full in the November number of the JOURNAL of the Institute, and therefore moved that they be approved as printed. The President stated that unless there was objection, this motion would be agreed upon. No objection was offered and the minutes were declared approved.

The Secretary then reported the following accessions and losses in membership since the last meeting: Four new Resident Members; one Life Member, who transferred from Resident Membership; one Non-resident Member who transferred from Resident Membership; and two deaths.

As there was no further Institute business to be transacted, the President announced that two John Scott Medals and Premiums were to be awarded to two of our members by the Board of Directors of City Trusts at this meeting, and then called upon Mr. Louis Heiland, Secretary of that body, to take charge of the meeting.

Mr. Heiland read the following statement:

JOHN SCOTT MEDAL FUND.

JOHN SCOTT, a chemist of Edinburgh, Scotland, in 1816, bequeathed to the City of Philadelphia, the sum of Four Thousand ($4000) Dollars, the income of which was to be "laid out in premiums to be distributed among ingenious men and women who make useful inventions, but no one of such premiums to exceed Twenty Dollars, and along with which shall be given a copper medal with this inscription 'to the most deserving.'"

Up until 1869 this Fund was administered directly by the City of Philadelphia. In that year the Assembly of the State of Pennsylvania passed an Act which provided that "the duties, rights and powers of the City of Philadelphia, concerning all property and estate whatsoever, dedicated to charitable uses or trusts, shall be discharged by the said City through the instrumentality of a Board, to be called Directors of City Trusts, consisting of twelve citizens, appointed by the Judges of the Courts of Common Pleas, to serve during good behavior, together with the Mayor of the City and the President of the City Council.

From that year—1869—until now, the John Scott Medal Fund has been under the care of the Board of Directors of City Trusts.

By an Ordinance of City Council, The Franklin Institute, in 1834, was appointed the agent for the distribution of awards under this trust. From that date—1834—until 1919, a period of eighty-five years, all awards were made upon the recommendation of The Franklin Institute, these awards totalling 361. In the Report of Common Council for the year 1837, it states:

"The employment of The Franklin Institute, as the agent for awarding the premiums, your Committee entirely approves, combining as that society does, an array of talent, science and public spirit, highly creditable to our City."

In 1919 the Fund had grown to $100,000, with an annual income equal to the amount of the original bequest. In that year the Board of Directors decided to appeal to the court for modifications of the terms as laid down by Mr. Scott.

By Decrees of the Court, the City of Philadelphia, Trustee, is authorized to distribute the income in premiums of the maximum value of $2000, to be accompanied by the usual copper medal, and to make such rules and regulations for enabling it to make a wise selection of beneficiaries, either by the selection of an advisory board, or otherwise, as it deems best; the premiums to be awarded for inventions that will be useful to mankind in the development of chemical, medical or any other science or development of industry in any form, the test being that the invention is, in the judgment of the trustee, definitely accomplished, and that it may add to the comfort, welfare and happiness of mankind.

Acting under the authority granted by the Court, the Board of Directors of City Trusts has formed an Advisory Committee, of three persons, nominated respectively by the National Academy of Sciences, the University of Pennsylvania and the American Philosophical Society. The present members of the Advisory Committee are:

Dr. H. H. Donaldson,
Dr. Arthur W. Goodspeed,
Mr. Samuel M. Vauclain.

The awards for 1927, as recommended by the Advisory Committee, are:

Dewey D. Knowles, Physicist, connected with the Westinghouse Electric and Manufacturing Company, of Pittsburgh, for the "invention of the grid glow tube." The presentation took place at a meeting, on October 13th, of the Pittsburgh Physical Society.

Afranio do Amaral, Director of the Antivenin Institute of America, for "the preparation of antivenins."

Alfred F. Hess, Clinical Professor of Children's Diseases, Columbia University, for "a method for producing a vitamin factor in food by ultra-violet light."

Peyton Rouse, Pathologist, Rockefeller Institute for Medical Research, for "a filtration technique separating from tumor cells of fowls a substance producing the disease."

These three gentlemen received the awards at a meeting of the Academy of Natural Sciences, November 1st, and the following two awards are to be made this evening:

Herbert E. Ives, B.S., Ph.D., Physicist, Bell Telephone Laboratories, New York, for "researches and inventions in electrical telephotography and television."

Strickland L. Kneass, C.E., Vice-president, William Sellers and Company, Inc., for "an exhaust steam injector, automatic operating and regulating

valves." (The purpose is to reclaim waste heat and to obtain the maximum temperature for the feed.)

He then asked Dr. H. E. Ives to stand, and said: I take pleasure in presenting to you on behalf of the Board of City Trusts, first the certificate, signed by the members of the Commission and the officers of the Board of City Trusts, the copper medal prescribed by Mr. Scott, and lastly, but by no means least, the check for $1000, premium award.

In receiving the Medal and Premium, Doctor Ives spoke as follows: Mr. Chairman, Ladies and Gentlemen: It is a great pleasure to me to receive *this medal* in this city and in this building. The reason that I emphasized this medal is a peculiarly personal one. One of my earliest recollections was seeing one of these medals in our family. My father, Mr. Frederick Ives, received one. When I was a small boy I conceived the hope that some day I might get one of these medals. What attracted me most as a small boy was the size and weight of this medal. Since then my ideas of the characteristics of this medal have changed, but I still take pleasure in receiving it.

I am glad to receive it in this city because it was in this city, in the basement of the Laboratory Building of the United Gas Improvement Company that I did the work on the production of light, the measurement of light, the utilization of light and finally on the photo-electric effect, which proved, after a time, to be the key to these problems of telephotography and television. It was in this Institute building and in this room that the results of these studies were presented for the first time.

I have just one more remark to make in this connection. In the early days when this medal was inaugurated, inventors worked alone. And in many cases independent inventors still work alone. Now times have changed. Scientific research, particularly in the industries, is carried out by team work. The big achievements are to be ascribed to organization rather than to ingenuity. Now that is particularly true of these achievements which are the subject of this award. The transmission of pictures by television could not have been brought to perfection without the many benefits of one of the big industries, and while it has been my great privilege to be so connected with this work that the award appears in my name, I accept it only with the distinct understanding that I am receiving it as a tribute to the Bell Telephone Laboratories and the large group of men who collaborated in this work.

Mr. Heiland then presented a John Scott Medal and Premium to Mr. Strickland L. Kneass in the following terms: I take pleasure in presenting this John Scott Medal Award, first the certificate, second the medal, and third the check for $1000, to Mr. Strickland L. Kneass, Vice-president, William Sellers and Company, Inc., for "an exhaust steam injector, automatic operating and regulating valves."

Mr. Kneass responded: Mr. Secretary, I desire to express to you and to the Board of City Trusts, my deep appreciation of the honor conferred on me. The purpose for which this award has been made is not as notable as that for which the award was made to Doctor Ives.

This system is composed of a number of coöperating and interdependent units: Primarily, the injector-heater; this is of non-lifting form and similar in appearance to the usual non-lifting type; it contains a set of low-pressure

tubes with an exhaust steam nozzle of large diameter which delivers the water from the tender tank, heated and containing a large percentage of exhaust steam, under pressure to a set of forcing tubes operated by steam from the boiler.

The injector-heater is connected to the exhaust passages of the cylinders of the engine, preferably to both the front and rear ends, so as to obtain an even flow. Intercepting this pipe is an automatic regulating valve which maintains a practically constant pressure and flow to the injector, independent of the amount of steam used in the cylinders. This valve is of special design, balanced against pressure and arranged so that it closes automatically when the engine throttle is shut, while a supplemental valve admits a supply of steam from the boiler to the injector to obtain continuous and uninterrupted feed to the boiler. All these motions are automatic and independent of control by the engine crew.

There is a further factor which is essential; during the starting of a heavy train the flow of exhaust steam is in irregular pulsations and it is not until a speed of about five miles an hour is attained that the flow to the injector is fairly regular. A further element has therefore been introduced, a retarding valve, which delays the shift from live to exhaust until the required continuity of flow has been reached. The final element completing the system is a simple form of starting valve operated by a lever in the cab for admitting steam from the boiler to the injector in requisite sequence, to the live steam admission valve and then to the forcing tubes of the injector.

The theoretical efficiency is based upon the increase of temperature of the water from the tender tank, due to the absorption of exhaust steam from the cylinders. This varies somewhat between summer and winter conditions, but it is and should be in excess of that due to the condensation of the live steam used for forcing the water into the boiler; the temperature of the feed to the boiler in service reaches 285° and in laboratory tests 300° F.

There are further resultant economies due to the high temperature of water entering the boiler. It is obvious that the almost complete elimination of expansion and contraction of the tubes and flue sheets tends to reduce boiler repairs, while the large storage of hot water, not far below the temperature of the steam permits emergency call upon the fire without materially increasing the stoking and waste of coal due to imperfect combustion. (Exhaust Tip.)

The inventions and improvements for which this distinguished award has been made contain elements which were discovered many years ago by an eminent French engineer, so that it seems fitting at this time to pay tribute once more to Henri Jacques Giffard, the inventor of the steam injector.

It is difficult for us to realize in this day of investigation and research how few of the elements were known in his generation of the present science of thermodynamics. The education received by Giffard at L'École Centrale was as complete as could be obtained by an aspirant to the degree of engineer, but it must be remembered that his graduation in 1849 was before Joule had obtained his valuation of the mechanical equivalent of heat, and two years before Rankine or Clausius published independently their epoch-making treatises covering the general law of thermodynamics. It was in this same year,

1851, seven years before the application for his patent, that Giffard, then a struggling and ambitious engineer, designed and made the drawings of a new form of boiler feeder which he named "The Injector." Full appreciation of his talent has been and still should be given, when is realized the small amount of data at hand and the embryonic condition of the science. His discovery of a new principle and his ability to deduce the laws governing the movements of a vapor and its fluid within conical guiding nozzles was a remarkable achievement.

Giffard was a pioneer. The problem of feeding a steam boiler under special limitations was presented to him. Boldly discarding the principle of the pump, he conceived the idea of using the energy and the latent heat of a vapor to raise and force many times its own weight of liquid into and against the pressure of its generator.

It is not necessary to review the means he employed to develop his conception but only to state that a French patent was granted to him in May, 1858, which covered the underlying principles of the most generally used boiler feeder of the present day.

During the decades which followed, modifications were made and new features added by Continental, English and American inventors, but there are few changes of importance which were not anticipated or suggested in the text of the patent specification or in his own "Treatise on the Injector," published in 1861.

Giffard did not, however, touch upon the use of exhaust steam or of a vapor at a lower pressure than that of its generator. As a factor of economy, the recovery of waste heat from the exhaust was as important in his time as in ours and many patents were issued covering its use. In the operation of railroads, fuel cost is one of the principal items and the proportion of heat units contained in the exhaust steam of a locomotive to the heat transformed into tractive effort is a large item. Inventors have attempted the solution of the problem in various ways and with more or less success, but it is obvious that an extension of the principle developed by Giffard, by which the impelling force of a jet of steam discharging into a partial vacuum produced by contact with its own fluid, meets most nearly the theoretical requirements of the utilization of the latent heat of the exhaust for refilling the boiler or generator by and with part of the waste product.

It is much simpler to state the problem than to solve; the varying conditions of locomotive service due to change of load, of the position of the throttle and cut-off, cause differences in supply and pressure, so that the main and newest problem has been to include the control of conditions under which the injector operates and to introduce self-regulating mechanism to maintain constant conditions of exhaust steam and feed supply. Upon American Railroads this is more essential than in English and Continental countries, by reason of the heavier train loads, great variety of service, and the steeper grades that obtain in this country.

My own interest in the use of exhaust steam commenced early in my work of experimental engineering, for in 1883 I designed a fixed nozzle type of atmospheric pressure injector capable of feeding a boiler carrying 75 pounds steam. This injector was not put in commercial use because the rapid introduc-

tion of the tubular stationary boiler led to the adoption of much higher steam pressures. All drawings, models and tests were preserved for future reference and proved of value in recent years.

It is illuminating to read and recall the prejudice against the introduction of Giffard's injector by railroad employes and the obstacles encountered in overcoming the deep-seated favor shown toward the old-fashioned pumps. It is difficult to wean men away from established habits; human nature does not change from generation to generation, but prejudice must give way to the march of progress; science and the mechanic arts go steadily forward, and, as in the past, will put in the shadow that which an earlier generation has regarded as an achievement.

Mr. Heiland expressed the appreciation of the Board of Directors of City Trusts for the courtesy of the Institute in arranging for the presentations at this meeting.

The President of the Institute then introduced as the lecturer of the evening Mr. A. H. Rudd, Chief Signal Officer of the Pennsylvania Railroad, who spoke delightfully on "Automatic Train Control and Other Safety Devices." The speaker made a very interesting comparison among the different devices which had been suggested for the promotion of safety in the operation of trains. His talk was heard with close interest and was followed by an animated discussion.

The meeting was adjourned at nine-thirty-two P.M.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting Held Wednesday, November 2, 1927.)

HALL OF THE COMMITTEE,

PHILADELPHIA, November 2, 1927.

MR. M. M. PRICE *in the Chair.*

The following reports were presented for final action:

No. 2867: Kinematic Computing Devices.

These devices employ kinematic methods in the solution of problems in electrical circuits and machinery. The names of several of these devices and the uses to which they are put are as follows:

(1) The Secomor, which enables the characteristics of a polyphase series commutator motor to be obtained.

(2) The Indumor depicting the performance of a polyphase induction motor.

(3) The C.P.S.'ER, which is a device for performing mechanically the vector computations continually occurring in alternating-current problems.

(4) The Heavisidion, which shows the voltage and current relations at any point of a long transmission line under various conditions of operation.

The award of the Elliott Cresson Medal to Prof. Vladimir Karapetoff, of Cornell University, was recommended.

No. 2873: Method of Making and Finishing Welded Pipe.

This process consists of passing pipes that have been butt welded through sets of horizontal and vertical rolls when the pipe is at such a temperature that the distortion caused by passing through the rolls, cracks off the adhering scale and leaves the pipe scale-free, both outside and inside.

The award of the Edward Longstreth Medal was recommended to Dr. Frank N. Speller, of Pittsburgh, Penna.

The following report was presented for first reading:

No. 2876: Permalloy.

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, November 9, 1927.)

RESIDENT.

MR. FREDERICK M. BRIGHAM, The Fairfax, 5501 Wayne Avenue, Germantown, Philadelphia, Penna.

MR. CHARLES W. HUNTER, Vice-president, U. G. I. Contracting Company, 1401 Arch Street, Philadelphia, Penna.

MR. LEWIS N. LUKENS, JR., Insurance Broker, 132 South Fourth Street, Philadelphia, Penna.

MR. HOWARD S. PAINE, Chemist, H. O. Wilbur and Sons, 235 North Third Street, Philadelphia, Penna.

CONTRIBUTING.

MR. FOSTER NOWELL, Engineering Department, The Bell Telephone Company, 1631 Arch Street, Philadelphia, Penna.

MR. R. L. SNYDER, Engineering Department, The Bell Telephone Company, 1835 Arch Street, Philadelphia, Penna.

TRANSFERS.

LIFE MEMBERSHIP FROM RESIDENT MEMBERSHIP.

MR. CONRAD H. BOLEY, Philadelphia, Penna.

MR. RICHARD G. SAGEBEER.

CHANGES OF ADDRESS.

DR. ROBERT J. ANDERSON, in care Fairmont Manufacturing Company, Fairmont, West Va.

MR. A. W. BERRESFORD, The Groovenor, 35 Fifth Avenue, New York City, N. Y.

MR. ARMIN ELMENDORF, The Celotex Company, 323-6 Australia House, Strand, London, W. C. 2, England.

MR. ARTHUR FALKENAU, The Lewises, Katonah, N. Y.

DR. PAUL D. FOOTE, Mellon Institute of Industrial Research, Pittsburgh, Penna.
MR. CHARLES N. FORREST, 1600 Arch Street, Philadelphia, Penna.
MR. J. DAWSON HAWKINS, P. O. Box 163, Colorado Springs, Colo.
MR. NATHANAEL G. HERRESHOFF, P. O. Box 116, Coconut Grove, Fla.
MR. J. C. JOHNSON, General Superintendent of Telegraph, Pennsylvania Railroad Company, 15 North Thirty-second Street, West Philadelphia, Penna.
MR. JULIAN D. JONES, Room 515, General Office Annex, Pennsylvania Railroad, 15 North Thirty-second Street, West Philadelphia, Penna.
DR. ISRAEL MAIZLISH, Professor of Physics and Mathematics, Head of the Department of Physics, Centenary College, Shreveport, La.
MR. ALBERT C. MIDDLETON, Room 606, Wilson Building, Camden, N. J.
MR. DAVID PELTON MOORE, 501 F Street, N. W., Washington, D. C.
MR. JOSEPH S. PECKER, 706 Chestnut Street, Philadelphia, Penna.
MR. T. MORRIS PEROT, JR., 132 Bethlehem Pike, Chestnut Hill, Philadelphia, Penna.
MR. EDWARD H. TAIT, 429 Main Street, Pen Argyl, Penna.
MR. EDWARD S. WOOD, JR., 2928 Rising Sun Road, Ardmore, Penna.
MR. JAMES A. WRIGHT, Wright Fischer Engineering Company, 798 St. Catherine Street, Montreal, West, Canada.
MR. RICHARD G. SAGEBEER, 703 Nottingham Road, Wilmington, Dela.

NECROLOGY.

Mr. Lewis Lillie, Philadelphia, Penna.
Mr. George Vaux, Jr., Bryn Mawr, Penna.
Mr. F. W. Weston, Wynnewood, Penna.

LIBRARY NOTES.

RECENT ADDITIONS.

American Electrochemical Society.—Transactions 1926, Volume 50. 1927.
Beilstein's Handbuch der organischen Chemie. Vierte Auflage, Zehnter Band. 1927.
BORELLI, JOHANN ALFONS.—Die Bewegung der Thiere. Übersetzt von Max Mengeringhausen. Ostwald's Klassiker der exakten Wissenschaften. Nr. 221. 1927.
Chemical Engineering Catalog. Twelfth annual edition. 1927.
CRANE, E. J., and AUSTIN M. PATTERSON.—A Guide to the Literature of Chemistry. 1927.
EDER, JOSEF MARIA, Ed.—Ausführliches Handbuch der Photographie. Volume 2, Parts 2 and 3. Two volumes. 1927.
FISHER, SYDNEY GEORGE.—The True Benjamin Franklin. 1902.
GEIGER, H., and KARL SCHEEL.—Handbuch der Physik. Band xviii. Geometrische Optik, optische Konstante, optische Instrumente. Redigiert von H. Konen. 1927.
Geologisches Zentralblatt. Generalregister zu Bände 16–30. 1927.

HAAS, ARTHUR.—Atomic Theory: an Elementary Exposition. Translated by T. Verschoyle. No date.

HUNTINGTON, ELLSWORTH.—The Human Habitat. 1927.

KOPACZEWSKI, W.—Les Ions d'Hydrogène. 1926.

MAYER, ROBERT.—Beiträge zur Dynamik des Himmels und andere Aufsätze. Herausgegeben von Bernhard Hell. Ostwald's Klassiker der exakten Wissenschaften. Nr. 223. 1927.

Philadelphia City Directory. 1927.

Royal Society of London.—Philosophical Transactions Series B. Volume 215. 1927.

STRONG, FRANK.—Benjamin Franklin: a Character Sketch. 1903.

Thomas' Register of American Manufacturers. Eighteenth annual edition. 1927.

University of Bombay.—Examination Papers 1925. 1927.

WIEDEMANN, G., and R. FRANZ.—Über die Wärmeleitungsfähigkeit der Metalle. Herausgegeben von Dr. Arthur Wehnelt. Ostwald's Klassiker der exakten Wissenschaften. Nr. 222. 1927.

ZSIGMONDY, RICHARD.—Kolloidchemie. Fünfte Auflage. II Spezieller Teil. 1927.

BOOK REVIEWS.

OILDOM. ITS TREASURES AND TRAGEDIES. By Oscar H. Reinholt. 383 pages and index unpaged, 8vo. Philadelphia, David McKay Co. Price, $4.

Pouring oil on troubled waters was for many years a suggestion of pacification, but within the last quarter of a century, oil has been most seriously troubling the waters of diplomacy. It seemed, indeed, in the years immediately following the Great War that as soon as some of the leading nations recovered financially, that is "got the price," they would go to fighting over oil control. Lately, rubber seems to be a source of trouble, but oil still holds a prominent place as an irritant.

The work in hand contains a very large amount of matter set forth in an interesting and lucid manner. The many oil fields of the world are described and the story is liberally illustrated. The fulminant manner in which many oil fields have been developed, giving rise to enormous fortunes quickly acquired and often as quickly lost through extravagance or the failure of supply, the feverish speculation that has so often carried many a humble investor into poverty from the loss of the savings of years; the disturbance of markets through overproduction: All these features make the story full of snap. Older readers of the book will recall "Coal-oil Johnny," and his meteoric career.

When the "War between the States," as the civil war of 1861–1865 is now often called, occurred, the seceding states thought that England would come to their aid for "cotton was king." Later when the use of steam for marine service became dominant, coal took a leading place, but the introduction of the oil burner for shipping and the vogue of the automobile with its demand for the lighter portions of petroleum have made marked changes and the end is not yet.

The book is recommended as a valuable compendium of data on all points of importance concerning the beneficial and the possible evil influences of the winning and use of petroleum. HENRY LEFFMANN.

THE HUMAN HABITAT. By Ellsworth Huntington, Yale University. xii–293 pages, 8vo. New York, D. Van Nostrand Company, Inc. Price, $3.

"What though the spicy breezes blow soft o'er Ceylon's isle,
Where every prospect pleases and only man is vile;
In vain with lavish kindness the gifts of God are strown,
The heathen in his blindness bows down to wood and stone."

In 1857, Thomas Henry Buckle published the first volume of a "History of Civilization" in which he argued with much force and many illustrations that the aspects of nature are the basis of the transformation of man from the savage to the civilized state. In 1867, Carl Marx published his book "Capital," largely determined by a study of the British industrial system, arguing that the dominant motive of mankind in communities is the economic, in other words, as Mr. Grewgious said to Rosa Bud, "Business is business." The philosophy of Marx has found concrete expression in the doctrine of the "materialistic conception of history."

The author of the book under review has been a prolific writer on topics covered in the work and related subjects. He has devoted much time and great industry to collecting the data, and has contributed much material which will arouse thought in the minds of his readers and contribute to a broader outlook on world affairs. He has an easy, attractive style which will contribute much to the popularity of the book, for after all it is the "man in the street" that needs education in such principles. Yet it may be a question whether this facile, attractive style may not have some disadvantage. The reader is carried forward so easily and comfortably that he may not stop to think whether all that is said is to be taken without hearing the other side. Not that our author has any intention to mislead. He seeks the truth and his purpose is to proclaim it, but a writer of broad information and powers of attractive expression may, as was said of Macaulay, write "his story" instead of "history."

The book surveys mankind from China to Peru; and from Greenland's icy mountains to India's coral strand. Afric's sunny fountains and the ancient rivers and palmy plains are not overlooked. The general conclusion agrees with that of Buckle, carried, of course, much further in detail and to a much greater degree of precision, owing to the immense amount of material that has become available in the seventy years that have elapsed since Buckle wrote. The general principle established seems to be that temperate climates, especially of the northern hemisphere, are best adapted to high civilization. In fact, it seems clear that unless there is a "snow line," that is, a season of fairly cold weather each year, mankind becomes lax and loses ambition. The denizen of such a climate may, indeed, in many places test this out for himself. Let him take a walk on a cold winter day, properly clad, and, if in fair health, he will soon find himself comfortably reacting to the condition, feeling warm and energetic. Let him now turn into a hothouse where ferns and other tropical plants are growing and very soon a listlessness will develop. The reviewer

has often made this experiment. A brisk walk for a mile or so in Fairmount Park on a cold day, and then enter Horticultural Hall, where the banana, tree fern, screw pine and similar plants are growing, and in a few minutes he feels like taking a siesta.

In considering works like the present, one is tempted to inquire as to what is civilization, what is progress, what is culture. Progress is defined by Huntington as increasing ability to control the forces of nature. Civilization might be taken as synonymous with culture and defined as an equal cultivation of the head and heart, that is, a development of knowledge with a coincident development of ethics and morals. In any study of the matter we must not overlook the fact that our modern civilization is so largely industrial that it is differentiated from all previous conditions which historians term civilizations. We can hardly compare the conditions in Assyria, Egypt, Greece, Judea, and Rome in ancient times with the great nations of to-day. It may, indeed, be a question whether all the extension of machinery has inured to human comfort as a total. "Rose bushes and poor rates as against steam engines and independence," said Macaulay in derision of Robert Southey's views, but many thinking persons are doubtful if the automobile, airplane, submarine, long-range cannon, high explosives, war gases and other products of the last fifty years of invention and discovery do more good than evil. Certainly this enormous progress did not prevent a most cruel and destructive war, and all signs to-day are that the great nations are preparing for another contest, one which will probably make the one just closed seem like a summer foray.

This book will appeal to all thinking people and it should find a very wide circle of readers. It would have been somewhat gracious if Buckle's book had been mentioned but Huntington's work is all his own and it is not likely that he derives any data from the earlier writer. In one respect he has made a fatal mistake, it is to be feared. On page 163 he tells us that the Loyalists of the Revolutionary period were, as a whole, people of "high character and ability." Wait until "Bill" Thompson and his factotum "Sport" Hermann see this statement. "Not for Chicago" will be the verdict. Such a dastardly attempt to put George III into America will doom the book to combustion on the Lake Front. The publisher will have to follow the method of biologies and natural histories and issue an edition properly expurgated.

It is interesting to note how completely the modern works of this character ignore the old view and accept, at least, tacitly, the theory of man's relationship to the rest of the animal world. HENRY LEFFMANN.

KOLLOIDCHEMIE, EIN LEHRBUCH. Von Richard Zsigmondy, Universität Göttingen. Vol. 2, special part, with a table and 16 illustrations. Fifth edition, revised and enlarged. x–256 pages, 8vo. Leipzig, Otto Spamer, 1927. Price, 14 marks.

The first part of this book covering the general physical chemistry of colloids was reviewed in this JOURNAL in 1925. The second part represents the same method of treatment of the subject but deals with the various materials in their colloidal condition. The amount of material now available in colloid chemistry is so great and the labor of collecting it from the literature and

presenting it in satisfactory form compelled the division of the work into two parts and has delayed the appearance of the second part.

The same principles of arrangement followed in the first part have been applied in the preparation of the second. In this present issue the reader will find many examples of the progress in knowledge on this subject and many paragraphs which are appendixes to the data given in the previous volume. References are also made to data in the third and fourth editions of the work. Almost everywhere one finds references to the significance of the primary and secondary particles (monone and polyone) for the structure and characteristics of colloid solutions and also the results of the exact investigation concerning the composition of the particles.

The preparation of the volume has been materially expedited by the services of collaborators whose work is gracefully acknowledged in the preface. Among these are Prof. Dr. Handovsky, of Göttingen, whose contributions are in the department of egg albumin colloids, and Doctor Thiessen, also of Göttingen, who has contributed to the article on soap as well as certain other chapters. Several of the collaborators have been especially helpful in connection with proof-reading and credit is also given to one of them for the careful verification of the index. Of the book, therefore, it can merely be said that it completes the work projected a couple of years ago and the two volumes constitute a comprehensive and highly valuable presentation of the data on this interesting and important, and yet decidedly abstruse, field of physical chemistry.

HENRY LEFFMANN.

OVERHEAD SYSTEMS REFERENCE BOOK. Prepared by a Special Committee of the Overhead Systems Committee, Engineering National Section, National Electric Light Association. 592 pages, illustrations, quarto. New York, National Electric Light Association, 1927. Price, $7.50.

This comprehensive work on the art of overhead transmission and distribution of electricity has only recently appeared from the press. Although it is, in a way, a successor to the "Handbook on Overhead Line Construction," last printed in 1914 and out of print for some years, the new book has been completely rewritten and rearranged. The principal subjects, aside from tables and general information, are in order, Wood Poles, Steel Poles, Towers and Substation Structures, Materials, Insulators, Transformers, Protective Apparatus, Street Lighting, Electrical and Mechanical Calculations, Methods of Construction, Meteorological Data, Tree Trimming and general safety suggestions.

All of these subjects are presented in such a manner that they are directly applicable to modern conditions and they have, therefore, a freshness and practical usefulness that is often lacking when old material has been reworked. Through selection of the most desirable methods that are employed in this important work in various sections of the country, it has been possible to present in tangible and readable form the most approved and satisfactory methods. Replete with illustrations, drawings and information, the work is the last word in present-day construction and maintenance.

Appearing at this time, this text-book on overhead power lines assumes an added importance in view of the research work on power transportation

started by the NELA during the last year in various universities. Using the methods shown in this book as a basis, the research engineers are further investigating the subject with the view of possibly improving on the practices that have so far been selected as the best. The work is well printed, on paper especially manufactured for it, and is bound in full flexible fabrikoid.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 270, The Measurement of Pressure through Tubes in Pressure Distribution Tests, by Paul E. Hemke. 11 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, ten cents.

The tests described in this report were made by the Committee to determine the error caused by using small tubes to connect orifices on the surface of aircraft to central pressure capsules in making pressure distribution tests.

Aluminum tubes of 3/16-inch inside diameter were used to determine this error. Lengths from 20 feet to 226 feet and pressures whose maxima varied from 2 inches to 140 inches of water were used. Single-pressure impulses for which the time of rise of pressure from zero to a maximum varied from 0.25 second to 3 seconds were investigated.

The results show that the pressure recorded at the capsule on the far end of the tube lags behind the pressure at the orifice end and experiences also a change in magnitude. For the values used in these tests the time lag and pressure change vary principally with the time of rise of pressure from zero to a maximum and the tube length. Curves are constructed showing the time lag and pressure change. Empirical formulas are also given for computing the time lag.

Analysis of pressure distribution tests made on airplanes in flight shows that the recorded pressures are slightly higher than the pressures at the orifice and that the time lag is negligible. The apparent increase in pressure is usually within the experimental error, but in the case of the modern pursuit type of airplane the pressure increase may be 5 per cent. For pressure distribution tests on airships the analysis shows that the time lag and pressure change may be neglected.

Report No. 271, Pressure Distribution Tests on PW-9 Wing Models Showing Effects of Biplane Interference, by A. J. Fairbanks. 13 pages, illustrations, quarto. Washington, Government Printing Office, 1927. Price, ten cents.

In this report tests are described in which the distribution of pressures over models of the wings of the PW-9 airplane was investigated. The wing models were tested individually and in the biplane combination. The investigation was conducted in the atmospheric wind-tunnel of the Committee. It is concluded in this paper that the effect of biplane interference on the pressures on the wings is practically confined to the lower surface of the upper wing and the upper surface of the lower wing; that the overhanging portion of the upper wing is not greatly affected by the presence of the lower wing; and that a slight washin at the centre section of the upper wing satisfactorily compensates for a reduced chord at this section (providing the air-foil section is not mutilated) and prevents a large reduction in the normal force over this portion of the wing.

PUBLICATIONS RECEIVED.

The Human Habitat, by Ellsworth Huntington. 293 pages, illustrations, 8vo. New York, D. Van Nostrand Company, 1927. Price, $3.

Oxidation—Reduction Reactions in Inorganic Chemistry, by Eric R. Jette, Ph.D. 152 pages, illustrations, 12mo. New York, The Century Company, 1927. Price, $1.10.

Lois Fondamentales de l'Électricité. Cours pratique d'électricité industrielle par MM. Léon Bouthillon and Goudonnet. 271 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1926. Price, 14 francs.

Cours pratique d'Électricité Industrielle, par Mm. Léon Bouthillon and M. Goudonnet. Deuxieme volume: Machines et appareils électriques. 324 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1927. Price, 20 francs.

A System of Qualitative Analysis for the Rare Elements, by Arthur A. Noyes and William C. Bray. 536 pages, 8vo. New York, The Macmillan Company, 1927.

U. S. Bureau of Mines: Mineral Resources of the United States, 1926, Part I, No. 1: Chromite in 1926, by J. W. Furness. 8 pages. No. 5: Tin in 1926, by J. W. Furness. 22 pages, illustrations. No. 7: Antimony in 1926, by J. W. Furness. 14 pages. Part II, No. 5: Asphalt and Related Bitumens, by G. R. Hopkins. 20 pages. No. 6: Salt, Bromine, and Calcium Chloride in 1926, by A. T. Coons. 10 pages. No. 7: Barite and Barium Products in 1926, by R. M. Santmyers and A. Stoll. 10 pages. No. 31: Coke and By-products in 1924, by F. G. Tryon and Others, with a report on the marketing of coal products by R. S. McBride. 137 pages, 8vo. Washington, Government Printing Office, 1927.

National Advisory Committee for Aeronautics: Technical Notes, No. 267, Pressure Distribution on Wing Ribs of the VE-7 and TS Airplanes in Flight, by R. V. Rode. 4 pages, illustrations. No. 268, Mass Distribution and Performance of Free-flight Models, by Max Scherberg and R. V. Rode. 25 pages, illustrations, quarto. Washington, Committee, 1927.

A Tale of Yesterday, To-day and To-morrow, by Floyd W. Parsons. A recital of business victories and tribulations and setting forth a business philosophy that has brought the Joseph Dixon Crucible Company through a hundred years of service. 32 pages, 12mo. Jersey City, The Joseph Dixon Crucible Company, 1927.

U. S. Bureau of Mines: Bulletin 260: The Ferric Sulphate-sulphuric Acid Process, compiled by Oliver C. Ralston with a chapter on producing small bubbles of gas in liquids by submerged orifices, by Chas. G. Maier. 122 pages, illustrations, 8vo. Price, 30 cents. No. 266: Technology and Uses of Silica and Sand, by W. M. Weigel. 204 pages, illustrations, plates, 8vo. Price, 40 cents. No. 286: Quarry Accidents in the United States during the Calendar Year 1925, by William W. Adams. 98 pages, 8vo. Price, 20 cents. Washington, Government Printing Office, 1927.

U. S. Bureau of Mines: Technical Paper 415, The Function of Steam in the Limekiln, by Ernest E. Berger. 43 pages, illustrations, 8vo. Washington, Government Printing Office, 1927. Price, ten cents.

CURRENT TOPICS.

The Influence of the Atmospheric Constituents on Climate. L. B. ALDRICH. (*Bull. Nat. Research Council*, No. 81, July, 1927.)—On April 28th and 29th there was held in Washington, D. C., the eighth annual assembly of the American Geophysical Union attended by scientific men from Canada as well as from the United States. At the Symposium on Some Factors of Climatic Control this paper was presented. "Climate is largely determined by the prevailing range of temperature. The temperature is maintained, first, by solar radiation which continuously falls upon our atmosphere at the mean rate of 1.93 calories per square centimetre per minute; and secondly, by the exceedingly complicated series of absorptions, scatterings, reflections, endless re-radiations, and convection and conduction effects which result from the passage of the solar beam through the atmosphere. Oxygen and nitrogen, which comprise the bulk of the atmosphere, have relatively little effect on temperature. Four other constituents, however, comprising less than 3 per cent. of the weight of the atmosphere, are highly important as affecting temperatures. These constituents are water (both as water vapor and in the form of clouds), dust, ozone, and carbon dioxide." On a clear day only about 75 per cent. of the radiation from the sun at the zenith comes directly through the atmosphere and reaches sea-level. Of the remaining 25 per cent. part is reflected out into space, part is scattered and comes to the earth as sky-light, and still another part is selectively absorbed, chiefly by water vapor. For any other altitude of the sun the path of its light in the air is longer. This reduces the fraction directly transmitted and increases the brightness of the sky. On hazy days the presence of water vapor or dust likewise makes smaller the directly transmitted radiation and makes larger the reflected, absorbed and scattered portions. "To illustrate the variation in intensity of the directly transmitted beam even in a cloudless sky and at altitude of 3000 metres above sea-level, I have chosen more or less at random the following observations on four different days at the Montezuma station of the Smithsonian Institution." (This table is here omitted.) "The first two days show that an increase of water-vapor content depleted the solar beam 7 per cent. The last two show that though the water-vapor content remained unchanged, an increase of dust sufficient to double the diffuse scattering also produced a 7 per cent. depletion. And comparing the first and third days, an 11 per cent. depletion is found in a hazy, moderately wet sky as compared with a dry, clear sky. On cloudy days practically no radiation is directly transmitted and more than 75 per cent. is reflected back to space from the upper surface of the cloud."

The temperature of the surface of the earth depends upon the relative magnitude of the solar radiation received in relation to the radiation emitted by the earth. It is the atmosphere, and not the solid earth, that is the chief source of the outgoing radiation. Since the earth is much lower in temperature than the sun, the outgoing radiation has, roughly speaking, fifteen times the wave-length of that coming from the sun. This marked difference in the character of the two streams of radiation causes them to be affected quite differently by the constituents of the atmosphere. "On a clear but humid day the absorption of solar radiation by water vapor would rarely be so great as 15 per cent. In contrast, water vapor absorbs terrestrial radiation almost completely, except in the region around 10μ, and even there it is partially absorbing. This 'greenhouse effect'—transmitting solar radiation but screening off the terrestrial—is still strong, even in a very dry atmosphere. This fact—that even a very small amount of water vapor so strongly absorbs terrestrial radiation—makes it evident that reasonable variations in the water-vapor content of the atmosphere would have little effect on climate." If, on the other hand, water is present in the atmosphere, not as vapor only, but also as cloud, change in the areas covered by clouds will modify terrestrial temperatures. Brooks estimates that, were the 50 per cent. of the earth's surface now on the average cloud-covered to be increased to 55 per cent., this change would be followed by a reduction of the mean annual temperature of the earth by 5°. The reason for this lies in the fact that the upper surface of a cloud reflects 78 per cent. of the solar radiation falling on it and thus reduces the energy reaching the earth's surface.

When volcanic eruptions discharge into the upper air huge quantities of dust, this is caught in the sweep of global air-currents and carried around the world. This was true of the Krakatoa eruption more than forty years ago and of the Katmai eruption of 1912. In the latter case observations made in Algeria and in California showed that the atmospheric transmission coefficients were reduced by 20 per cent. Like water vapor, dust particles absorb more of the terrestrial than of the solar radiation, but Humphreys has shown that their major effect comes from scattering and reflecting and not from absorption. He computes that dust in the prevention of the passage of radiation is thirty times as effective for solar as for terrestrial emission. He designates this as the "inverse greenhouse effect." This tends to lower the earth's temperature. "Brooks computes that the 20 per cent. reduction in the atmospheric transmission coefficients such as occurred in the Katmai eruption of 1912, if long continued, would lower the mean temperature of the earth over 5° C. On the other hand, he points out that the complete absence of volcanic dust would not raise the mean much over ½° C., an amount insufficient to account for the temperatures which prevailed during warm geological epochs."

With regard to carbon dioxide in the atmosphere, it seems that

its amount might vary over a wide range without much resultant change in the temperature of the earth's surface. The rôle of ozone is imperfectly understood. According to Fabry this substance in the upper atmosphere may absorb 4 per cent. of the incident solar radiation. In addition ozone possesses an absorption band at about 10μ near the wave-length at which terrestrial radiation has its maximum of energy and at which it happens that water vapor has its weakest absorption. Thus the presence of ozone accentuates the "greenhouse effect," which opposes the result caused by the absorption of radiation from the sun by the same substance in the upper regions of the atmosphere. The author concludes that there are three possible changes in the composition of the atmosphere which, sufficiently prolonged, would cause distinct changes in climate:

"(1) A change in total cloudiness, provided all other factors remained unchanged.

"(2) An increase in fine dust. This would effectively lower the temperature.

"(3) A large increase in the amount of ozone in the upper air would probably effectively lower surface temperatures. As yet, however, exact data are unavailable regarding the formation of atmospheric ozone and regarding its ability to transmit radiation."

G. F. S.

Currents Carried by Point-discharges beneath Thunderclouds and Showers. T. W. WORMELL. (*Proc. Roy. Soc.*, A 771.)—This paper presents the results of observations extending over a period of eight months, chiefly in the year 1926, and conducted in the Solar Physics Observatory, Cambridge, England. It describes "experimental methods employed for investigating the sign and magnitude of the vertical current due to the point-discharge of electricity from an elevated metal point, during the intense electric fields associated with thunderstorms and showers." The discharging point mounted on a pole was 8.3 metres above the ground. The apparatus for current measurements was in a hut from which a cable ran to the point. For a short distance the insulation was of quartz so that usually rainfall failed to affect it.

Two methods were used to measure the current discharged from the point. In the first a voltmeter with dilute sulphuric acid integrated the quantities of electricities traversing the circuit. By having the gas collect in tubes .8 mm. in diameter, the author obtained a bubble of hydrogen 2.5 mm. long for the passage of one coulomb, and was able to measure quantities of electricity from .01 coulomb upward with an accuracy of .001 of the unit. If the current changed its direction, bubbles of mixed hydrogen and oxygen were formed. From the volume of these it was easy to calculate the quantity of electricity that had passed in each direction, though the momentary variations could not be followed. The voltmeter was put in circuit between the discharge-point and the earth. In the second method,

the connections of which are too lengthy to be here described, the current was computed by counting the number of sparks passing in unit time across an air gap of .3 mm. A capillary electrometer of the C. T. R. Wilson form joined in parallel to the spark gap made it possible to follow the progress of charging and even to register it by photographing the position of the meniscum in the electrometer. "As a storm approaches, the magnitude of this current may increase in a few seconds from something undetectable (a value less than, say, 10^{-10} ampere) to 10^{-5} ampere or more, a range of values of 1 to 10^5. The method of observation adopted has the advantage that measurements are possible over a very wide range of values of the current, and that no damage will be done to the apparatus by currents of unexpected magnitudes."

There is tabulated the results of observations made on something over sixty cases of showers, snowfall, thunderstorms, etc. The showers were generally not long, lasting about thirty minutes. In two instances described as "Persistent gentle rainfall" and "Fairly heavy rain," both in April, 1926, no transfer of electricity between the point and the air was found, and there were two later similar absences of flow. In seven other cases only traces of current were detected. In ten cases in the course of the observations the same quantity of positive electricity was discharged from the point into the air as came from the air to the point. In seven instances less positive electricity escaped into the air than was received from it, but in no case was the quantity in either direction very considerable, the maximum transfer having occurred in a "Prolonged steady rain" when 5 millicoulombs left the point and 7 entered it. In all these seven instances there was some upward movement of positive electricity. The total transfer to the air was 16 millicoulombs and that from the air 33. Thirty-two times the quantity of positive electricity escaping exceeded that received. It was not uncommon that none whatever was received. Once in a heavy thundershower 30 millicoulombs escaped while none was received. In all the more than sixty observations made, 255 millicoulombs went upward and 82 passed in the opposite direction. In fine weather there is an ionization current downward through the air amounting to 2×10^{-12} ampere per sq. m. "It will be seen from the table that it was frequently found that, during a heavy shower, lasting, perhaps, thirty minutes, a net quantity of positive electricity of the order of 10 millicoulombs was discharged from the earth by the single point under observation. Such a quantity will neutralize the fine weather current into an area of about 160 square metres during a whole year. These figures will, perhaps, suffice to indicate the importance of the effect investigated. It is clear that in any discussion of the total transfer of electricity between the earth and the atmosphere, the effect of the point-discharge currents from prominent natural objects, such as trees, during periods of intense electric field, cannot be neglected. One would expect the results obtained with the appa-

ratus described to be of the same order of magnitude as the quantity of electricity discharged, under the same conditions, from a small tree." G. F. S.

Milton Whitney, 1860–1927.—Professor Whitney, internationally known soil scientist and chief of the Bureau of Soils of the U. S. Department of Agriculture from the time of its organization in 1894 to June of this year, died at his home in Takoma Park, Md., early on the morning of November 11th. Although he retired as active chief last June, he continued his research work in the bureau to the end.

Professor Whitney was born in Baltimore, Md., August 2, 1860, and received his early education in the Baltimore schools. Three years of special work in chemistry at Johns Hopkins University, under the direction of the famous chemist, Dr. Ira Remsen, inspired him to give his attention to the study of soils and their relation to plant growth. Concluding his studies at Johns Hopkins in 1883, he was made assistant chemist of the Connecticut Agricultural Experiment Station. In 1886 he became superintendent of the experiment farm of the North Carolina Experiment Station where he acquired much practical experience in the handling of soils which was of great value to him in his later scientific studies. It was in the report of his work at this station that he first called attention to the profound influence of the physical properties of soils upon crop production.

In 1888 he accepted the positions of professor of agriculture in the University of South Carolina and vice-director of the experiment station. In 1891 Professor Whitney went to the Maryland Experiment Station and while there the Weather Bureau of the Department of Agriculture placed certain funds at his disposal that he might complete a full report on soil investigations. This was published as Weather Bureau Bulletin Number 4.

The Department of Agriculture was so influenced by the necessity for study of the great problems of the soil as set forth in Professor Whitney's bulletin that it established a Division of Soils in 1894 and he was selected as its head. The work of the early division grew until Congress set it up as a bureau in 1901 with Professor Whitney as chief. Under his direction the work of the bureau expanded greatly and covered many lines of investigation. He established the Soil Survey, an organization having for its objective the mapping of the soil-types of the entire United States. This undertaking has proved its worth and to-day more than one-third of the arable lands of the United States have been painstakingly mapped to show the extent and location of the various types of soil.

Early in its history the Bureau of Soils undertook a study of the alkali problem of the western lands and a method was devised for the reclamation and handling of alkali soils. Under Professor Whitney's direction also the study of soils suitable for tobacco rais-

ing was inaugurated, and it was he who was chiefly instrumental in the establishment of tobacco growing under shade in the Connecticut River Valley. He directed the governmental work on the fixation of atmospheric nitrogen; and in 1911, when there arose the threat of a German monopoly of the potash supply, he threw his organization enthusiastically into the field for the development of adequate domestic sources of potash and other fertilizer materials.

His prominence in the field of soil science was probably never more adequately recognized than at the opening of the First International Congress of Soil Science held in Washington this summer. The Congress paused at its opening meeting to adopt a resolution of regret that Professor Whitney was unable to attend because of his illness, and to acknowledge his place as a soil scientist of international reputation.

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